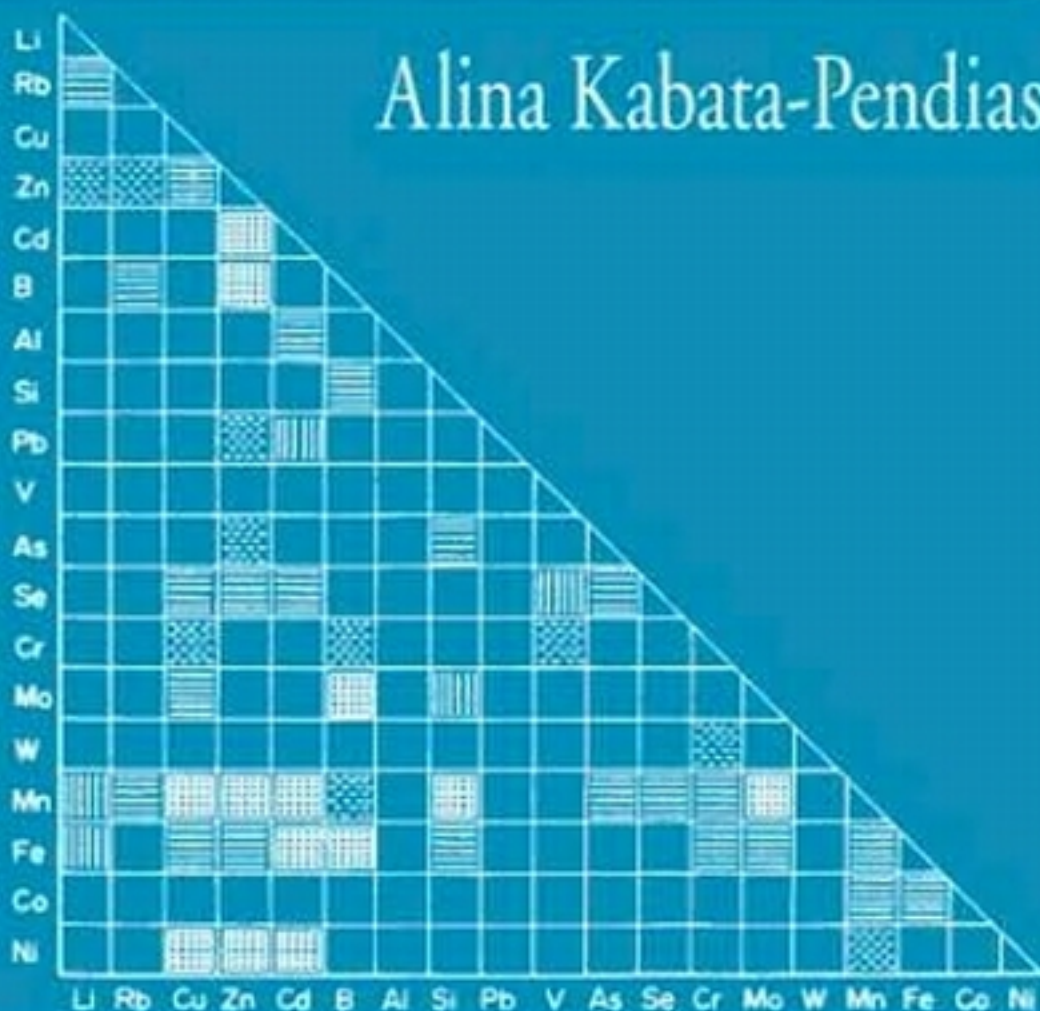


Trace Elements in Soils and Plants

Fourth Edition

Alina Kabata-Pendias



CRC Press
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*Dedicated to the memory of my husband, Henryk Pendias,
coauthor of the first and second editions*

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Symbols

PRESENTATION OF DATA

The basic units of the International System (SI Unit) are used as units in this book. Mean contents—refer to arithmetic mean value, unless otherwise specified.

The concentration of a trace element in soil, plant, animal, and human samples is based on the total content by weight of the element in air-dried or oven-dried (at 40°C) material. Otherwise it is indicated as follows: (1) AW—ash weight and (2) FW—fresh or wet weight.

All data are given for topsoils, unless otherwise indicated. If not identified, a content of an element in environmental samples is given as, the so called “total,” that is, measured in totally digested sample or measured directly in a sample.

UNITS

Mt	million metric tons (10^3 kt)
Kt	thousand metric tons (10^3 t)
t	metric ton (10^3 kg)
kg	kilogram (10^3 g)
g	gram (10^{-3} kg)
mg	milligram (10^{-3} g)
μ g	microgram (10^{-3} mg)
ng	nanogram (10^{-3} μ g)
pg	picogram (10^{-3} ng)
fg	femtogram (10^{-3} pg)
ppm	μ g/g = mg/kg = g/t
ppb	10^{-3} ppm = ng/g = μ g/kg = mg/t
ha	hectare ($10,000$ m ²)
L	liter (1 dm ³)
mL	milliliter; 10^{-3} L
m ³	cubic meter (10^3 dm ³)
Bq	becquerel
mBq	millibecquerel
Ci	curie; 1 Ci = 3.7×10^{10} Bq
mCi	millicurie
nCi	nanocurie
pCi	picocurie
$t_{1/2}$	half life-time of a radionuclide
pm	picometer (10^{-12} m); $1 \text{ \AA} = 100$ pm
kJ	kilojoule (unit of energy)

THE PERIODIC TABLE OF ELEMENTS

The symbols given in thin letters indicate the elements not occurring naturally in the environment

1																	18
¹ H	2											13	14	15	16	17	² He
³ Li	⁴ Be											⁵ B	⁶ C	⁷ N	⁸ O	⁹ F	¹⁰ Ne
¹¹ Na	¹² Mg	3	4	5	6	7	8	9	10	11	12	¹³ Al	¹⁴ Si	¹⁵ P	¹⁶ S	¹⁷ Cl	¹⁸ Ar
¹⁹ K	²⁰ Ca	²¹ Sc	²² Ti	²³ V	²⁴ Cr	²⁵ Mn	²⁶ Fe	²⁷ Co	²⁸ Ni	²⁹ Cu	³⁰ Zn	³¹ Ga	³² Ge	³³ As	³⁴ Se	³⁵ Br	³⁶ Kr
³⁷ Rb	³⁸ Sr	³⁹ Y	⁴⁰ Zr	⁴¹ Nb	⁴² Mo	⁴³ Tc	⁴⁴ Ru	⁴⁵ Rh	⁴⁶ Pd	⁴⁷ Ag	⁴⁸ Cd	⁴⁹ In	⁵⁰ Sn	⁵¹ Sb	⁵² Te	⁵³ I	⁵⁴ Xe
⁵⁵ Cs	⁵⁶ Ba	⁵⁷ * La	⁷² Hf	⁷³ Ta	⁷⁴ W	⁷⁵ Re	⁷⁶ Os	⁷⁷ Ir	⁷⁸ Pt	⁷⁹ Au	⁸⁰ Hg	⁸¹ Tl	⁸² Pb	⁸³ Bi	⁸⁴ Po	⁸⁵ At	⁸⁶ En
⁸⁷ Fr	⁸⁸ Ra	⁸⁹ ** Ac	¹⁰⁴ Rf	¹⁰⁵ Db	¹⁰⁶ Sg	¹⁰⁷ Bh	¹⁰⁸ Hs	¹⁰⁹ Mt									

* Lanthanide series

⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	⁷¹ Lu
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** Actinide series

⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es	¹⁰⁰ Fm	¹⁰¹ Md	¹⁰² No	¹⁰³ Lr
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Abbreviations

AAAc	ammonium acetic acid
AAAcEDTA	mixture of ammonium acetic acid with Na ₂ EDTA
AAP	acid available particulate
AD	Alzheimer's disease
ADI	acceptable daily intake
ADP	adenosinediphosphate
AHM	Asian herbal medicines
AIEA	International Atomic Energy Agency
AMAP	Arctic Monitoring and Assessment Programme
A/N	ratio of anthropogenic to natural sources
AROMIS	Assessment and Reduction of Heavy Metal Inputs into Agro-Ecosystems
ASB	alkaline-stabilize biosolids
ASM	Artisanal and small-scale gold mining
ATP	adenosinetriphosphate
ATSDR	Agency for Toxic Substances and Disease Registry
AW	ash weight
BAC	biological absorption coefficient
BAT	biological tolerance values at workplace
BC	before Christ
BCF	biological concentration factor
BIM	biologically induced minerals
BP	before the present time (used in expressing geological time)
B-x	blood level of a given element
Cc	continental crust concentration of element
CEC	cation exchangeable capacity
Clarke	Clarke's data for mean values for chemical elements in a given geological material
CLPP	community level physiological profile
COPR	chromite-ore processing residue
Cw	dissolved concentration of element in water
Cw/Cc	ratio of element concentration in water to its content in the continental crust
DBT	dibutyltin
DDI	daily dietary intake
DMT	dimethyltin
DM-X	dimethylated element
DNA	de(s)oxyribonucleic acid, carrier of genetic information
DOC	dissolved organic carbon
DOM	dissolved organic matter
DTPA	diethylenetriaminepentaacetic acid
DU	depleted uranium
DW	dry weight

EC	European Commission
EDTA	ethylenediaminetetraacetic acid
EF _c	enrichment factor-ratio of element concentration in air to its content in the Earth's crust, normalized to the reference element (Al)
EPA	Environmental Protection Agency
ESADDI	estimated safe and adequate daily dietary intake
FA	fulvic acid
FAO	Food and Agriculture Organization of the United Nation
FDA	Food and Drug Administration
FMI	free metal ion
FW	fresh weight
GEMS	Global Environment Monitoring System
GERM	Geochemical Environmental Reference Methods
GIS	geographical information system
HA	humic acid
HELCOM	Helsinki Commission
HDL	high-density lipoproteins
HI	hazardous index
HRE	heavy rare earth
HS	humic substances
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
IBA	index of bioaccumulation
ICRP	International Protection Commission on Radiological Protection
IDD	Iodine Deficiency Disorders
IHC	Interactive Health Communication
IHR	International Health Regulation
IPCS	International Program on Chemical Safety
IUPAC	International Union of Pure and Applied Chemistry
IUR	International Union of Radioecology
JECFA	Joint FAO/WHO Expert Committee on Food Additives
KBD	Kashin–Beck disease
KD	Keshan disease
LAs	lanthanides
LDH	low-density lipoproteins
LDL ₀	the lowest lethal dose
LDL ₅₀	lethal dose, the simple dose of an element which causes the death of 50% of a population in a specific period of time
LOAEL	lowest-observed-adverse-effect level
LRE	light rare earth
LTI	lowest threshold intake
MAC	maximum allowable concentration
MAK	maximum concentration of a chemical substance on air at the workplace (in German)

MBT	monobutyltin
MCL	maximum concentration level
MCRA	Monte Carlo Risk Assessment
Me-X	methylated metal
MF	modifying factors
ML	maximum level
MMT	methylcyclopentadienyl manganese tricarbonyl
MM-X	monomethylated metal
MND	motor neurone disease
MPC	maximum permissible concentration
MPL	maximum permissible limit
MSW	municipal solid waste
MTD	maximum tolerable dose
MTL	maximum tolerable level
NAS	National Academy of Sciences
NIOSH	National Institute for Occupational Safety and Health
NOAEL	no-observed-adverse-effect level
NOEC	no observed-effect concentration
NOM	natural organic matter
NP	nanoparticles
OECD	Organization for Economic Cooperation and Development
OEL	occupational exposure limit
OM	organic matter
OSHA	Occupational Safety and Health Administration (in United States)
OTC	organo-tin compound
PbB	lead in blood
PCBs	polychlorinated biphenyls
PGE	platinum group element
PGM	platinum group metal
PLFAs	phospholipids fatty acids
PM	particulate matter (e.g., PM ₁₀ = particle 10 µm in diameter)
PMTD	provisional maximum tolerable daily intake
PR	phytoextraction rate
PT ₅₀	phytotoxicity threshold corresponding to 50% growth retardation
PTDI	provisional tolerable daily intake
PTWI	provisional tolerable weekly intake
RDA	recommended dietary allowance
RDB	relative deviation to background
RDI	recommended daily intake
REE	rare earth element
RfD	reference dose
RMSE	square root of the variance of the residuals
RNA	ribonucleic acid, structural element of the cytoplasm and cell nucleus
SeCys	selenocysteine
SeGSH	selenoglutathione
SeMC	selenomethylocysteine

SeMet	selenomethionine
SETAC	Society of Environmental and Toxicological Chemistry
SOD	superoxide dismutase
SOM	soil organic matter
SPTF	soil–plant transfer factor
TAV	trigger action value
TBT	tributyltin
TDI	total dietary intake
TDS	Total Diet Study
TE	trace element
TEA	triethanolamine
TF	transfer factor (ratio of an element content in plant to its concentration in soil)
TI	tolerable intake
TIC	trace inorganic contaminants
TLV	threshold limit value
TM	trace metal
TUIL	tolerable upper intake level
TWA	time weighted average
UF	uncertainty factors
UL	tolerable upper intake level
UNEP	United Nations Environmental Program
UNESCO	United Nations Educational, Scientific and Cultural Organization
UPAC	International Union of Pure and Applied Chemistry
USEPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
VEC	vehicle
WHO	World Health Organization
W/S	worms/soil concentration ratio

Preface

A decade has passed since the third edition of *Trace Elements in Soils and Plants* (CRC Press, 2000) was published. During this period there has been tremendous explosion in research and public interest related to trace elements in the environment. Cycling of chemical elements is through fundamental processes that control life on our planet. The transfer of chemical elements through the food chain is a part of natural cycling. However, several anthropogenic factors have changed the natural and balanced supply, especially of trace elements to food and forage. An incredible number of publications have been focused on the significance of the chemical balance for a safe environment and for human health.

I have tried to continue the goal that has been set for three earlier editions of this book, which was to provide a brief but informative introduction to the biogeochemistry of trace elements in the soil–plant system. The fourth edition incorporates up-to-date data from more than 1500 recent sources, selected from a much higher number of publications that have appeared in the twenty-first century. These increased data on trace elements are due to a growing understanding of their importance as both essential elements and toxic elements, as well as due to recently developed instrumental analytical methods (e.g., ICP-MS, MC-ICP-MS, ICP-OES, F-AAS, ETA-AAS). New analytical methods have also given more data on elements previously barely investigated, such as lanthanides and actinides.

New data are especially selected to present the current knowledge on trace elements associated with topics such as: (1) soil natural/background contents; (2) sorption/desorption processes; (3) anthropogenic impact and soil phytoremediation; (4) phytoavailability and functions in plants; and (5) contents in food plants.

Although the term “trace elements” has never been defined precisely, I do prefer to use it instead of other terms, especially of the term “heavy metals,” which is very confusing because it is based on various criteria and has never been defined by any authoritative body (Duffus 2002).

Trace elements are presented in this edition of the book in a new order, according to the recent IUPAC recommendation.

I do hope that information added to this edition of the book will be useful to those who are concerned about the chemical quality of the environment and will encourage both young scientists and students to study the biogeochemistry of trace elements in greater depth.

Alina Kabata-Pendias

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Authors

Alina Kabata-Pendias, PhD, DSc, Professor Ordinary of Environmental Geochemistry was head of the Trace Elements Laboratory of the Institute of Soil Science and Plant Cultivation in Puławy, Poland for more than 30 years. Today, after 60 years at the Institute in Puławy, she holds the title of Professor Emeritus. She also worked for 30 years at the Polish Geological Institute in Warsaw on the mobility of trace elements and on the alteration of minerals in weathered zones of various geological formations.

Professor Kabata-Pendias' research interest has been always focused on the fate of trace elements in the soil–plant chain. She has published about 320 papers, articles, and book chapters. She has authored (together with husband, Henryk Pendias) three books, including *Trace Elements in Soils and Plants*, published by CRC Press. The first edition of this book was published in 1984 (in five prints, 1985–1988), the second edition was published in 1992, and the third edition in 2001. The first edition of this book was translated by “Mir” to Russian in 1989. Two other books were written in Polish: one (*Trace Elements in Biological Environment*) was edited by the Geological Publisher in 1979, and the second (*Biogeochemistry of Trace Elements*) was published by PWN in 1993 and in 1999. The fourth book, coauthored by A.R. Mukherjee (*Trace Elements from Soils to Human*) was published by Springer in 2007.

Professor Kabata-Pendias has been active in several national and international scientific organizations and committees, such as FAO, SCOPE, UNESCO, ISTEb, and MAB. She has also served as an invited reviewer of numerous manuscripts submitted to international journals and is currently serving on the editorial board of *Environmental Geochemistry and Health*. She has been awarded several prestigious medals, including most recently the Phillipe Duchafour Medal, bestowed by the European Geosciences Union.

Henryk Pendias, PhD, the coauthor of the first and second editions of this book, passed away in 1994.

For 28 years, Dr. Pendias was head of the Department of Petrography and Geochemistry of the Polish Geological Institute in Warsaw. He had been a member of the staff of this institute since 1950. His geochemical studies resulted in more than 60 publications, including three books. The main subjects of his research were the distribution of trace elements in various geological formations and the impact of biogeochemical processes on the mobility of elements in geological environments. He also devoted much time and attention to methodical and analytical studies in geochemistry.

Dr. Pendias was a founding member of the Mineralogical Society of Poland and attended many national and international meetings.

Introduction

The quality of human life depends on the chemical composition of food and of the surroundings. Recent improvements and new methods in analytical chemistry and increasing fields of environmental investigations have added substantially to our knowledge of the biogeochemistry of trace elements. Over the last three decades there has been a real “explosion” of research data and various publications on occurrence and behavior of almost all trace elements including both elements of known and unknown physiological functions in organisms. In order to realize the vast significance of the biogeochemistry of trace elements, it is essential to gather the knowledge acquired over this period into one comprehensive compilation.

Soil is not homogenous, and the microscale heterogeneity creates a real problem in representative sampling. Also the variability in sampling procedure from plants and other organisms is a subject of concern and this has made the assessment and evaluation of some data almost impossible. Therefore, quantitative comparisons of analytical data for soils, plants, and human/animal tissues have often been difficult.

Different chemical preparations of samples (e.g., HNO_3 microwave decomposition, ashing with aqua regia, total digestion) as well as different instrumental methods used for the determination of elements (e.g., ICP-MS, ICP-OES, F-AAS, ETA-AAS) have an influence on final results. Luckily, analytical quality assurance and the use of reference materials have decreased uncertainties of analytical data. Therefore, each measurement of trace elements builds up a database and contributes to a better understanding of their overall distribution and behavior in given media and in the total environment.

A better understanding of the biogeochemical processes that control trace element cycling and comprehensive dataset on the abundance of trace elements in abiotic and biotic environmental compartments may be a key to better management of trace elements in the environment that is a prerequisite to sustainable land use and, presumably, to diminish health risks due to trace inorganic pollutants.

The term “trace elements” has never been defined precisely. It has been used in geochemistry for chemical elements that occur in the Earth’s crust in amounts less than 0.1% (1000 mg/kg) and also in biological sciences, for elements at similar concentrations. Therefore, some elements that are “trace” in biological materials are not “trace” in terrestrial ones (i.e., iron). The term “trace elements” is related to their abundance and includes elements of various chemical properties: metals and metalloids.

Common trace cation descriptors are “trace metals” and/or “heavy metals.” The trace metalloids are simple “trace elements.” The other terms: “micronutrients,” “essential elements,” and “toxic elements” are related to their physiological functions and are rather confusing since their effects on organisms and health depend upon concentrations. All these terms are inadequate, and a great deal of confusion has occurred in the literature where authors have been imprecise in their use of these terms. Especially the term “heavy metals” has recently become a subject of a broad discussion that emphasizes its nonprecise definition. Duffus (2002) has written: “Over the past two decades, the term ‘heavy metals’ has been widely used ... and related to chemical hazards. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity.” This term is based on various criteria (i.e., atomic weight, atomic number, density, chemical properties, etc.). Thus, the inconsistent use of the term “heavy metals” reflects inconsistency in the scientific literature. This term has never been defined by any authoritative body, such as IUPAC.

Other terms that need to be defined are related to chemical speciation and fractionation of elements. Thanks to new developments in analytical instrumentation and methodology, the identification and measurement of element species in a particular system is possible. In an attempt to end the confusion regarding the usage of the term speciation, three IUPAC Divisions collaborated to consider the issue (Templeton et al., 2000). Their definitions for the recommended use of term speciation are the following:

- *Chemical species*. Chemical elements—specific form of an element defined as per isotopic composition, electronic or oxidation state, and/or complex or molecular structure.
- *Speciation analysis*. Analytical chemistry—analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample.
- *Speciation of an element, speciation*. Distribution of an element among defined chemical species in a system.
- *Fractionation*. Process of classification of an analyte or a group of analytes from a certain sample according to physical or chemical properties.

1 The Biosphere

The biosphere, also called the ecosphere, is the natural environment of living things, the complex biological epidermis of the Earth, and its dimensions are not precisely defined. It consists of the surficial part of the lithosphere, a lower part of the atmosphere, and the hydrosphere. The chemical and physical characteristics of the biosphere are determined by these other spheres, which have created relatively constant environments that allow the existence of living matter in an ecosystem. The ecosystem is a fundamental environmental system consisting of the community of all living organisms in a given area and having a balanced cycle of chemical elements and energy flow. There is a homeostatic interrelationship between the nonliving (abiotic) environment and living organisms (biotic environment).

In general, the biosphere consists of three main ecosystems: a terrestrial environment, a freshwater environment, and a marine environment. These fundamental ecosystems include several smaller systems of variable dimensions and conditions. A significant part of the ecosystems has already been considerably modified by man, and such modification will continue.

The energy of life is derived from the radiant energy of the sun, which drives the chemical reaction of photosynthesis. The other sources of energy, such as geothermal energy, gravitation, and electric potential, are of negligible importance in the total energy flow; however, they may determine some of the conditions of ecosystems.

The beginning of life on Earth, according to one of the existing theories, may be due to adsorption of organic molecules by silicates and aluminosilicates. Montmorillonite, in particular, exhibits, in some gel forms, the ability to synthesize proteins. Yushin and Khlubov¹⁵⁶⁷ discovered the presence of various amino acids (glutamine, glycine, alanine, histidine, etc.) in montmorillonites found in hydrothermal deposits. These montmorillonite minerals are enriched in several trace elements, including Be, Mn, Cu, Zn, Pb, Ti, Sr, Ba, F, and REEs. The structural variability of silicate chains and their susceptibility to bind with organic compounds due to piezoelectricity are believed to be processes that stimulate the beginning of life.^{1450a}

Biochemical processes that produce organic matter in the Earth's environment are dated from the Early Precambrian Period, that is, over 3×10^9 years BC. The entire process of photosynthesis has been calculated to have developed about 1.5×10^9 years BC. Since that period, several million kinds of living organisms have evolved and adjusted to their natural environments.

Most mineral nutrients for all life on land are supplied mainly from the soil overlying the surficial lithosphere. The atmosphere is a source of only some of the essential nutrients (N_2 , O_2 , and CO_2) and the hydrosphere is the main source of water, a basic constituent of all life.

More than 90% of all living matter is composed mainly of organic compounds and water. Organomineral compounds and mineral compounds form a relatively small portion of living matter. The bulk of living matter is formed from the chemical elements C, O, H, and N. Such elements as K, P, Ca, Mg, S, Na, and Cl are present in living organisms in smaller and variable amounts. All these elements are readily mobile in the biosphere and are known to form either volatile or easily soluble compounds that are involved in major environmental cycles.

Many elements occur in trace amounts in living matter. Some of these elements are essential for the growth, development, and health of organisms. Usually, the quantitative difference between essential amounts and a biological excess of these elements is very small. Some trace elements seem to be essential to vital processes, but their biochemical functions have not yet been understood. The essentiality of other trace elements may be discovered in the future.

The chemical composition of living matter has developed and adjusted to the chemistry of environments over long periods of geologic time. However, all organisms, in order to survive in the complex geochemical composition of their surroundings, had to develop mechanisms to actively select elements involved in vital processes and reject a toxic excess of other elements. These processes are fundamental for homeostasis, which is essential for the existence of every organism.

Although all living organisms, and plants in particular, show a natural ability to select chemical elements, they are also highly dependent on the geochemistry of their surroundings. Any environmental factor that has an adverse effect on plants may cause either evolutionary or drastic changes even over short periods of time, involving only a few generations in the life of a plant species. These phenomena are easily observed in the evolving tolerance of populations, especially of microorganisms, to high concentrations of trace elements in either natural geochemical provinces or under human-induced conditions. This evolution of the biosphere is fully described in Williams' statement¹¹⁸⁵: "The evolution of the biosphere through natural selection resulted in organisms adapted to chemistry of the environment" (Williams¹¹⁸⁵).

Although biological selection of chemical elements allows plants to control their chemical composition to a certain extent, these controls are somewhat limited with respect to trace elements. Therefore, concentrations of trace elements in plants are often positively correlated with the abundance of these elements in soils and even in underlying rocks. This correlation creates several problems for plants, animals, and humans, problems associated either with a deficiency or an excess of trace elements. The questions surrounding how, and how much of, a trace element is taken up by plants from their environment have been topics of active research in recent years. At a time when food production and environmental quality are of major concern to humans, a better understanding of the behavior of trace elements in the soil–plant system seems to be particularly significant (Figure 1.1).

Biological processes depend on the flow of energy and elements (Figure 1.1). Energy from the sun is a fundamental factor that drives all reactions governing the transfer of elements among the environmental compartments. Global biogeochemical cycles are crucial for the survival of life on Earth in its present form, and the major biogeochemical cycles have been studied extensively.⁹⁴⁹ Each essential element in various forms flows from the nonliving (abiotic) to the living (biotic) components of the biosphere and back to the nonliving again. These cycles vary from one element to another, but each cycle consists of basic phases: gaseous, solution, and sedimentary. Cycles can

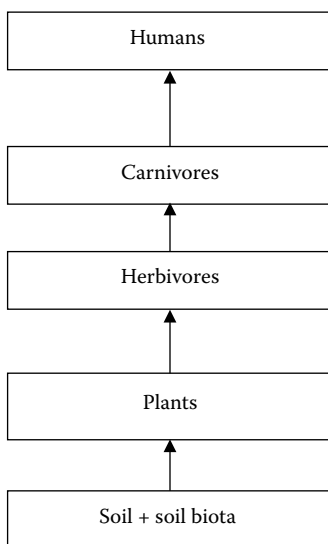


FIGURE 1.1 The transfer of chemical elements in a schematic terrestrial trophic chain.

be considered as having an exchange pool (mobile stage of an element) and a reservoir pool (immobile stage of an element). A reservoir pool is related to a sedimentary phase, and includes soil.

Trace element cycles are closely associated with major element cycles, but are much less understood. Some recent data on trace element behavior in both the natural environment and that modified by human activities have been reviewed by several authors.^{922,1137,1155}

Soil is not only a part of the ecosystem, but also plays a fundamental role in human survival, which is tied to the maintenance of its productivity. Soil has very important and complex functions as filter, buffer, storage, and transformation systems, protecting the global ecosystem against the effects of pollution. These functions of soil are not unlimited, but will remain effective so long as the soil's properties and natural balance are preserved.

2 The Anthroposphere

I INTRODUCTION

The role of man in the biosphere has been so important recently that it has become necessary to distinguish the anthroposphere—the sphere of man's settlement and activity. The anthroposphere (sometimes called technosphere), however, does not represent a separate sphere, but it can be applied to any part of the biosphere that has been changed under an influence of technical civilization.

Man's impact on the biosphere has been very broad and complex, and it has most often led to irreversible changes. Primitive man interfered little with relatively stable relationships within his environment. A growing capability of man to alter his surroundings and to control several natural processes is a source of drastic changes altering the balance of fragile natural systems based upon the balanced flow of elements and energy (Figure 2.1). While geological and biological alterations of the Earth's surface have been very slow, changes introduced and/or stimulated by man have accumulated extremely quickly in recent years. All man-made changes disturb the natural balance of each ecosystem that has been formed evolutionarily over a long period of time. Thus, these changes most often lead to a degradation of the natural human environment. Since the development of agricultural activities, several ecosystems have been altered into artificial agroecosystems. Although man's impact on the biosphere dates back to the Neolithic Period, the problems of the deterioration of ecosystems due to pollution became increasingly acute during the latter decades of the twentieth century.

During the course of evolution and life, organisms have adjusted to the chemistry of their environment and have developed their biochemistry in close connection to the composition of the natural environment. These phenomena have been easily observed mainly in microorganisms and plant population. Although mechanisms of biological selection of chemical elements allow plants to control, to a certain extent, their chemical composition, this barrier is somewhat limited in respect to trace elements. Therefore, concentrations of trace elements in plants are often correlated with the abundance of these elements in growth media.

Environmental pollution, especially by chemicals, is one of the most effective factors in the destruction of biosphere components. The most detrimental anthropogenic impact on the biosphere is related to emissions of various acids (e.g., H_2SO_3 , H_2SO_4 , HF , HNO , and HNO_3) and radionuclides. For example, according to Yanshin,¹⁵⁶¹ 769 technogenic accidents occurred on the Earth in 1992, of which 4.7% released different pollutants, mainly acids and radionuclides, to the atmosphere.

Among all chemical contaminants, trace elements are believed to be of a specific ecological, biological, and/or health significance. Cawse⁹⁶⁰ emphasized that the interactions between gaseous pollutants and atmospheric trace metals are an important consideration; for example, the phase oxidation of SO_2 to SO_4^{2-} is catalyzed by Mn, and the formation of HNO_2 aerosol from NO_2 is increased by Cu, Mo, and Zn. Many textbooks have been published on trace elements as pollutants in the biosphere or in particular ecosystems, and all have pointed out the triangular relationships between contents of inorganic trace pollutants in air, soil, and plants.

Energy and mineral consumption by man is the main cause of trace element pollution in the biosphere. An estimation of the global release of trace elements as contaminants into the environment may be based on the established world mineral and energy consumption. The amounts of most trace metals deposited due to anthropogenic activities on the surface of the Earth are often greater

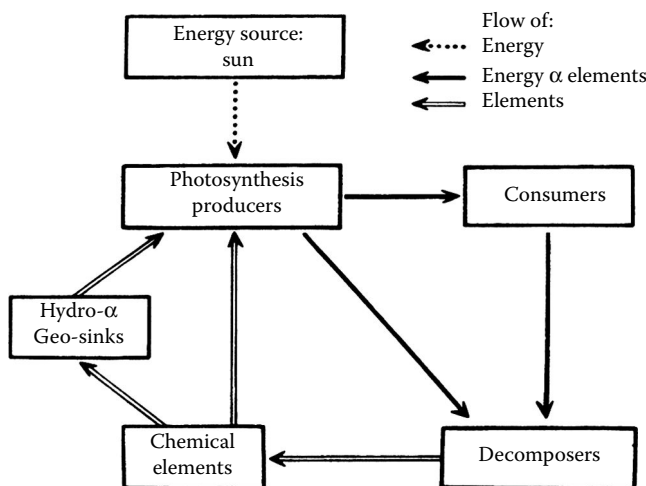


FIGURE 2.1 Schematic model of chemical element transport and energy flow in the environment.

than depositions from natural sources. Combustion processes are the most important sources of some metals, particularly, power generation, smelting, incineration, and the combustion engine.

Over the last decade an increase in metal mining is observed (e.g., Cr, Pb). For some elements the increase is by a factor of above 2 (Table 2.1). It is noteworthy, however, to emphasize that the highest increase has been noticed in crude oil production and hard coal production over the past two decades. Bowen⁹⁴ has suggested that when the rate of mining a given element exceeds the natural rate of its cycling by a factor of 10 or more, the element must be considered a potential pollutant. Thus, the potentially most hazardous trace metals to the biosphere may be Ag, Au, Cd, Cr, Hg, Mn, Pb, Sb, Sn, Te, W, and Zn. This list does not correspond closely to the list of elements considered to be of great risk to environmental health—As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, Tl, V, Zn, and some Lanthanides and Actinides.

Present-day soils contain trace elements of various origins. *Lithogenic* elements are those that are directly inherited from the lithosphere (mother material). *Pedogenic* elements are of lithogenic origin also, but their concentration and distribution in soil layers and soil particles are changed due to pedogenic processes. *Anthropogenic* elements are all those deposited into soils as direct or indirect results of man's activities. There have been assumptions that the behavior of trace elements in soils and in consequence their bioavailability differ as to their origin.^{381,469} Several recent findings, however, have clearly indicated that regardless of forms of the anthropogenic metals in soils, their phytoavailability is significantly higher than those of pedogenic origin.^{1019,1255,1357} Thus, it is most likely that under similar soil conditions, both lithogenic and pedogenic trace elements will be less mobile and less bioavailable than anthropogenic elements (Figure 2.2). Migaszewski et al. (2005) used the ANOVA calculation system for the assessment of the variability of S and trace elements in soils and plants and concluded that contents of these elements were controlled mainly by the parent material lithology and to a lesser extent by anthropogenic factors. Based on the ANOVA system, Oliva and Espinosa (2007) confirmed that the main pollution source of Ba, Cu, Ni, and Pb was traffic and fertilizers, whereas Cd, Fe, Mn, Ti, and V were attributed to natural sources.

Trace elements released from anthropogenic sources have entered the environment and have followed normal biogeochemical cycles. The transport, residence time, and fate of the pollutants in a particular ecosystem have been of special environmental concern. The behavior of trace elements in each ecosystem is very complex and therefore has usually been studied separately for air, water, soil, and biota. The urgent environmental problem at the present time is closely associated with

TABLE 2.1^{a,b}**World Mining of Elements in 2003 and 2008 (t, kt, Mt/year)**

Element	2003	2008	Element	2003	2008
Aluminum, Al (Mt)	148	39.7	Lithium, Li (kt)	41.6	27.0
Antimony, Sb (kt)	155	165	Manganese, Mn (Mt)	24.35	14.0
Arsenic, As (kt)	27.9	35.5	Mercury, Hg (t)	1530	950
Barium, Ba (kt)	80	7.700 ^c	Molybdenum, Mo (kt)	125	212
Beryllium, Be (kt)	3.8 kt	0.18	Nickel, Ni (Mt)	1.36	1.61
Bismuth, Bi (kt)	3.8 kt	5.8	Niobium, Nb (kt)	27	60
Boron, B (Mt)	4.4	4.1	Palladium, Pd (t)	230	206
Bromine, Br (kt)	551	398	Platinum, Pt (t)	192	200
Cadmium, Cd (kt)	16.87	20.8	Rhenium, Re (t)	38.0	57
Cesium, Cs (Mt)	5.9	—	Selenium, Se (kt)	2.01	1.59
Chromium, Cr (Mt)	15.83	21.5	Silver, Ag (kt)	19.1	20.9
Cobalt, Co (kt)	44.3	71.8	Strontium, Sr (kt)	366.7	512
Copper, Cu (Mt)	13.68	15.7	Tantalum, Ta (kt)	1.36	0.815
Fluorine, F (kt)	4.80 ^d	5.84 ^d	Thallium (t)	15	10
Gallium, Ga (t)	203	—	Tellurium, Te (t)	500	38 ^e
Germanium, Ge (t)	50 t	—	Tin, Sn (kt)	257.7	333
Gold, Au (kt)	2.57	2.33	Titanium, Ti (Mt)	4.22	6.29 ^f
Hafnium, Hf (t)	335	—	Tungsten, W (kt)	62.1	54.6
Indium, In (t)	310	568	Uranium, U (kt)	35.37	—
Iodine, I (kt)	21.4	27.0	Vanadium, V (kt)	49.2	60
Iron, Fe (Mt)	571	—	Zinc, Zn (Mt)	9.27	11.3
Lead, Pb (Mt)	3.00	3.8	Zirconium, Zr (Mt)	1.1	1.36

^a *Metal Statistics Yearbook 2004*, USGS (2004).

^b *Mineral Commodity Summaries*, USDI (2009).

^c Given as BaSO₄ (barite).

^d Given as fluorspar.

^e Data for Canada and Peru, only.

^f Given as TiO₂.

pollution in which trace metallic pollutants play a significant role. Ramade¹¹²⁵ made a lapidary statement that the problem of pollution was too long ignored by the industrialized nations. Recently developed procedures of life cycle assessment (LCA) and life cycle energy analysis (LCEA) control and evaluate environmental damage assignable to a product and/or service.

The principal criteria used to estimate trace element threats are: bioaccumulation, toxicity, and persistence. Evaluating environmental persistence in trace element contamination is the most difficult. It is commonly referred to as half-lives of an element in a given environment. Webster et al.¹⁵⁴⁰ discussed the feasibility of applying half-life criteria and emphasized the need for full consideration of such approaches.

II AIR POLLUTION

Most air pollution has arisen from the burning of coal and other fossil fuels and from smelting of iron and nonferrous metals. The steady global increase of trace element concentrations in the atmosphere is illustrated in [Table 2.2](#). Some trace pollutants, most likely Se, Au, Pb, Sn, Cd, Br, and Te, can exceed 1000 times their normal concentration in air. In general, elements that form volatile compounds, or are present at a lower particle radius, may be readily released into the atmosphere

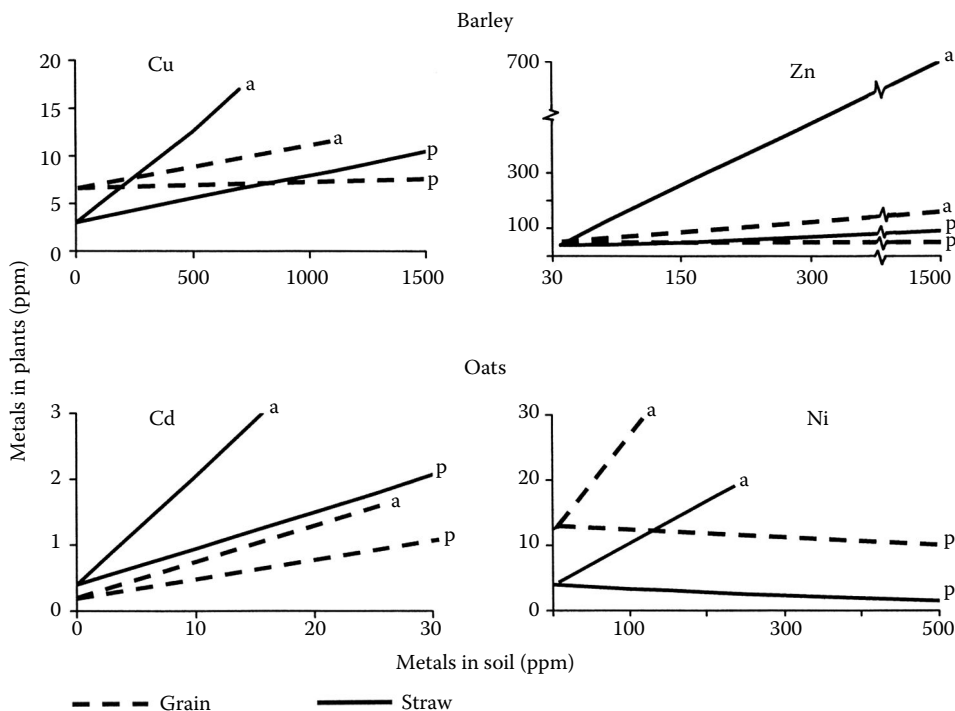


FIGURE 2.2 Trace metal uptake by barley and oats as influenced by the metal's origin, presented as multiple linear regression. Sources of metals: (a) anthropogenic, and (p) pedogenic. (Modified from Chlopecka, A., *Water Air Soil Pollut.*, 69, 127, 1993 and Grupe, M. and Kuntze, H., *Mitt. Disch. Bodenkundl. Gesellsch.*, 55, 333, 1987.)

from the burning of coal and other industrial processes. Materials released by man's activities are not the only contribution to global air pollution; some natural sources such as eolithic dusts, volcanic eruptions, evaporation from water surfaces, and others should also be taken into account. Buat-Ménard⁹⁵⁷ calculated that emissions of trace elements in the Northern Hemisphere are several times higher than in the Southern Hemisphere and are about 80% and 30%, respectively, of anthropogenic origin. A sharp increase in technogenic fluxes of trace elements has occurred in recent times.

Retrospective studies of trace element enrichment in ice layers, ombrotrophic peatlands, and tree rings show a steady increase of several trace metal contents due to anthropogenic emissions. However, recent observations have shown downward trends for several metals, for example, Fe, Pb, Cr, Cd, Hg, As, and Be. A significant reduction of Pb content in airborne particulates has recently been reported for some urban sites (Puxbaum and Limbeck, 2004).

The atmospheric deposition of trace elements, mainly the trace metals, contributes to contamination of all other components of the biosphere (e.g., waters, soils, and vegetation). This deposition has been widely reviewed, especially by Folkson,²³⁸ Jenkis,¹⁰³⁷ and Thomas,⁷⁸⁰ and Rühling and Tyler (2004), and it has been established that mosses and lichens are the organisms most sensitive to atmospheric pollution by trace metals, although sensitivity varies decidedly among species (Table 2.3). Gałuszka (2007b) reported that trace element accumulative capabilities of mosses differ depending on moss species and on plant communities; there are higher concentrations of Fe, Sr, Ti, Cr, Mo, Ni, and V in mosses from dry pine forest and increased concentrations of B, Mn, Rb, and Sb in mosses from continental coniferous forest. The author explained this phenomenon by various productivities of forests that affect cycling of elements. Pine needles also serve as bioindicators. Based on the chemical composition of *Pinus nigra* needles, Lehnendorff and Schwark (2008) concluded that the

TABLE 2.2
Trace Elements in Air from Different Locations

Element (ng/m ³)	Europe					America		
	South Pole	Greenland	Norway	West Germany	Japan	North	Central	South
Al	0.32–0.81	240–380	32	160–2900	40–10,600	600–2330	760–880	460–15,000
As	0.007	—	1.9	1.5–53	0.3–120	2–40	—	—
Be	—	—	—	0.9–4	5–100	0.1–0.3	—	—
Br	0.38–1.41	14–20	4.4	30.5–2500	1.6–150	6–1200	65–460	2–200
Cd	0.015	0.003–0.63	—	0.5–620	0.5–43	1–41	—	—
Cr	0.003–0.01	0.6–0.8	0.7	1–140	1.3–167	5–1100	1–2	1–8
Cu	0.03–0.06	—	2.5	8–4900	11–200	3–153	70–100	30–180
Fe	0.51–1.19	166–171	48	130–5900	47–14,000	829–2000	554–1174	312–9225
I	0.08	—	0.6	3–15	6	40–6000	—	—
Mn	0.004–0.02	2.8–4.5	3	9–210	5.3–680	60–900	14–16	4–330
Mo	—	—	—	0.2–3.2	—	1–10	—	—
Ni	—	—	1.2	4–120	1–150	120	—	—
Pb	0.19–1.2	15–22	—	120–5000	19–1810	45–13,000	0.2–317	11–344
Sb	0.001–0.003	0.9–45	0.3	2–51	0.13–63	1–55	0.8–15	1–24
Sn	—	—	—	1.5–800	—	10–70	—	—
Ti	—	—	2.6	22–210	5–690	10–230	—	—
V	0.0006–0.002	0.8–1.4	1.9	5–92	1.5–180	4–174	7–200	7–91
Zn (pg/m ²³)	0.002–0.051	18–41	10	550–16,000	14–6800	88–741	60–182	25–1358
Ce	0.8–4.9	—	60	360–14,000	100–18,000	20–13,000	—	—
Co	0.1–1.2	70–150	60	390–6790	44–6000	130–2200	250–650	120–360

continued

TABLE 2.2 (continued)
Trace Elements in Air from Different Locations

Element (ng/m ³)	Europe					America		
	South Pole	Greenland	Norway	West Germany	Japan	North	Central	South
Cs	—	—	20	60–1500	16–1500	70–300	—	—
Eu	0.004–0.02	—	—	5–80	7.3–27	10–1700	—	—
Hf	—	40–60	—	300	18–590	0.5–290	60–70	40–760
Hg	—	40–80	10	170–11,200	1600	70–3800	70–120	70–690
In	0.05	—	—	30–360	1200	20–140	—	—
La	0.2–1.4	50–110	30	610–3420	53–3000	490–9100	440	290–3400
Sc	0.06–0.21	30–40	5	30–700	5–1300	80–3000	150–220	60–3000
Se	4.2–8.2	170–360	260	150–11,000	160–21,000	60–30,000	280–1210	50–1530
Sm	0.03–0.09	10–12	3	240–420	9.8–320	70–1000	30–80	30–630
Ta	—	10–30	—	—	6–100	50–280	20–50	20–150
Tb	—	1–5	—	10	—	19–34	8–27	20–120
Th	0.02–0.08	20–40	11	30–1000	16–1300	50–1300	10–20	30–1050
U	—	—	—	20 ^a	—	<500	—	—

Source: Data compiled from various sources, mainly Bowen, H. J. M., *Environmental Chemistry of the Elements*, Academic Press, New York, 333, 1979; Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 300, 1979 (Po); Kitagishi, K. and Yamane, I., eds., *Heavy Metal Pollution in Soils of Japan*, Japan Science Society Press, Tokyo, 302, 1981.

^a Median value for Europe.

TABLE 2.3
Concentration of Trace Elements in Mosses Growing in Scandinavia (mg/kg)

Element	1990–1995 ^a	2000 ^b	Element	1990–1995 ^a	2000 ^b
Ag	0.037	0.02	Mn	310	289
Al	380	—	Mo	0.23	0.11
As	0.23	0.12	Nb	0.11	0.08
Ba	31	15.2	Nd	0.49	0.28
Be	0.023	0.011	Ni	3.6	0.65
Bi	0.033	0.0016	Pb	8.6	4.2
Cd	0.18	0.18	Pr	0.13	0.04
Ce	1.1	0.36	Rb	13	30.9
Co	0.37	0.12	Sb	0.15	0.11
Cr	2.6	0.79	Se	0.39	0.22
Cs	0.26	0.51	Sm	0.1	0.025
Cu	7	4.5	Sn	0.25	0.09
Dy	0.07	0.019	Sr	15	9.9
Er	0.037	0.011	Tb	0.013	0.004
Eu	0.02	0.01	Te	0.0052	—
Fe	660	—	Th	0.07	0.039
Ga	1.1	0.09	Ti	53	8.5
Ge	1.1	0.015	Tl	0.12	0.066
Gd	0.095	0.028	Tm	0.0048	0.001
Hf	0.0084	0.005	U	0.05	0.015
Hg	0.075	0.051	V	2.8	1.2
Ho	0.013	0.004	W	0.093	0.023
La	0.55	0.19	Y	0.31	0.1
Li	0.22	0.11	Yb	0.032	0.009
Lu	0.0042	0.001	Zn	45	32.2
			Zr	0.35	0.2

^a *Hylocomium splendens*. After Berg, T. and Steinnes, E., *Sci. Total Environ.*, 208, 197, 1997.

^b *Pleurozium schreberi*. After Rühling A., Tyler G. 2004. *Environ. Pollut.* 131:417–423.

most reliable indicators for sources of atmosphere pollution were REEs for lithogenic dust; Sb, Fe, and V for traffic; Mo and Pb for petrochemical emission; and Cd for mining activity.

Metals in the atmosphere, whether anthropogenic or natural in origin, are associated mainly with particles, except for Hg, which occur mostly in gaseous state. These elements are absorbed by particles, both inorganic and organic, mainly of diameter between 0.01 and 100 μm (NP). Particles of larger diameter have a tendency to precipitate quickly near the discharge source, but particle sizes less than 10 μm and low density may exist in the air from days to months and may be transported to distant regions. Trace elements of anthropogenic sources are widely distributed in the atmosphere and occur at high latitudes in mountains and in the Arctic. The atmospheric deposition of these elements, both wet and dry, contributes to the worldwide contamination of all environmental compartments. Trace metal deposition has been reported even for relatively remote sites, in rural areas across New Zealand (Gray et al., 2003). The amounts of most trace metals deposited on the surface of the Earth are usually greater than depositions from natural sources (Table 2.4). Combustion processes are the most important sources of trace metals, particularly, power generation, smelting, incineration, and the combustion engine. The nonferrous metal industry also contributes highly to the worldwide air pollution (Nriagu and Pacyna, 1988).

TABLE 2.4

Worldwide Emission of Trace Metals from Natural and Major Anthropogenic Sources to the Atmosphere (kt/year)^a

Element	SFFC ^b	Iron Industry	Nonferrous Metal Industry	Waste Disposal	Natural
As	0.81	0.35	3.45	0.12	12
Cd	0.69	0.06	22.17	0.04	1.3
Cr	10.15	2.83	—	0.43	44
Cu	7.08	0.14	18.07	0.62	28
Hg	1.48	0.03	0.16	0.11	2.5
Mn	9.42	1.06	0.06	0.51	317
Ni	86.11	0.04	8.88	0.13	30
Pb	11.69	2.03	14.82	0.82	12
Sb	0.73	0.007	0.55	0.27	2.4
Se	4.10	0.007	0.47	0.02	9.3
V	240.08	0.07	0.008	0.02	28
Zn	9.42	2.12	40.87	1.93	45

^a After Pacyna J.M., Pacyna E.G. 2001. *Environ. Rev.* 9:269–298.

^b SFFC—stationary fossil fuel combustion.

The environmental characteristics of inorganic trace pollutants in air are the following:

- Wide dispersion and long-distance transport
- Bioaccumulation, most often affecting the chemical composition of plants without causing easily visible injury
- Reaction in living tissues by disturbing the metabolic processes and by causing the reduction of sunlight entering plant tissues
- Resistance to metabolic detoxification, therefore entering the food chain

Indirect effects of air pollutants through the soil are of real importance because of the large-scale sustained exposure of soils to both wet and dry deposition of trace elements. These environmental effects should also be given greater attention. Release of trace elements from soils and basement rocks should also be considered as their source in air. The Pb, Sr, and Nd isotopic composition of biomonitors (lichens, etc.) from remote areas of Vosges mountains (France) is similar to that of granitoid basement rocks (Geagea et al., 2008). This indicates a direct impact of soils/rocks on the abundance of some elements in surrounding air.

There is a growing attention for Hg in the atmosphere, its sources and effects on ecosystems. Several models for regional and global assessment of Hg in the atmosphere have been proposed (Pirrone and Mason, 2008). Recent calculations presented in the report edited by these authors for Hg global release (in t/year) are: (1) 5207 from the natural sources (mainly from oceans and biomass burning), and (2) 2503 from anthropogenic sources (mainly biomass burning and artisanal gold mining production).

III WATER POLLUTION

Trace elements are present in natural waters (ground and surface), and their sources are associated with either natural processes or man's activities. The basic natural processes contributing trace

elements to waters are chemical weathering of rocks and soil leaching. Both processes also may be largely controlled by biological and microbiological factors. The anthropogenic sources of trace elements in waters are associated mainly with mining of coal and mineral ores and with manufacturing and municipal waste waters. Water pollution by trace elements is an important factor in both geochemical cycling of these elements and in environmental health. The hydrocycle is the “cross-road” chain of trace element fluxes in each ecosystem and terrestrial ecosystem as well.¹¹³⁷ Ecological consequences of trace element pollution of waters are difficult to assess because, on the global scale, they are also likely to promote unpredictable geochemical processes.

Most trace elements, especially trace metals, do not exist in soluble forms for a long time in waters. They are present mainly as suspended colloids or are fixed by organic and mineral substances. Thus, their concentration in bottom sediments or in plankton is most often an adequate indication of water pollution by trace elements. As Dossis and Warren¹⁹¹ concluded, sediments may be regarded as the ultimate sink for trace metals that are discharged into the aquatic environment. On the other hand, easily volatile elements such as Br and I can reach higher concentrations in surface waters, from which they can also readily vaporize under favorable climatic conditions. Microbial alkylation of the group of metals including Hg, Se, Te, As, and Sn that occurs mainly in sediments and on suspended particles in waters is also of great importance in their mobility.³⁵⁹

Korzh¹³⁶⁹ estimated the global transfer of the elements from oceans via the atmosphere on the continents. Yearly deposits of elements, grouped according to amounts, is as follows, in t/year (major elements are in parentheses):

1: Be, In, Eu, Tb, Tm, Lu

10: Sc, Co, Ge, Nb, Ag, Sn, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, Hf, Ta, Re, Au, Hg, Pb

10²: Cr, Mn, Fe, Cu, Ga, Se, Y, Zr, Cd, W, Tl

10³: Al, Ti, V, Ni, Zn, As, Sb, Cs, U

10⁴: Li, Rb, Mo, I, Ba, (N, P)

10⁵: B, F, (Si)

10⁶: Br, Sr, (C)

10⁷: (Mg, S, K, Ca)

10⁸: Cl, (Na)

This is clear evidence that the transfer in the water–air–soil chain plays a very significant role in elemental cycling.

The contribution of anthropogenic trace pollutants is very high for many sea basins. As Matschullat¹⁴⁰⁴ calculated, the fluxes of metals to the Baltic Sea from anthropogenic sources of both river flow and atmospheric deposition amount to over 90% of total input of Cd, Hg, and Pb, and about 80% of Cu and Zn. Trace elements concentrations in river waters might be very variable between both rivers and seasons and affect global riverine fluxes (Table 2.5).

Both phytoplankton and vascular water plants are known to selectively concentrate trace elements. For example, the highest accumulation by mezoplankton is observed for Cd, Cu, and Zn, while seaweeds take up Cd, Zn, Mn, and Pb more readily.¹⁵¹² As a result of this selectivity, concentrations of some trace elements in waters may decrease in some seasons, while other elements may become soluble during the decay of plants. Concentrations of trace elements in both bottom sediments and aquatic plants of streams are known to be a useful tool in biogeochemical exploration and environmental research. Soluble fractions of trace cations are rapidly caught either by clays or organic compounds and deposited in bottom sediments, or they are absorbed by root tissues of aquatic plants. Thus, concentrations of trace metals in these samples of the aquatic compartment reflect geochemical anomalies of the bedrocks and different anthropogenic sources of pollutants. The biochemical mapping of Sweden, based on aquatic plants, includes quite a number of trace elements: As, Au, Ba, Cd, Cl, Co, Cr, Cu, Hg, Mo, Nb, Ni, Pb, Rb, Se, Sr, U, V, W, Y, and Zn.^{953,1128}

TABLE 2.5
Trace Elements in River Waters and World Average Riverine
Fluxes to Oceans and Seas

Element	River Waters ^a , µg/L	Riverine Fluxes ^b , kt/year
As	0.13–2.71	23
Ba	3–80	860
B	1.5–150	380
Be	0.0006–0.61	0.33
Co	0.02–0.43	5.5
Cd	0.0006–0.42	3
Cr	0.29–11.46	5.5
Cu	0.23–2.59	55
Fe	31–739	2470
Li	0.16–4.5	69
Mn	1.3–50.7	1270
Mo	0.04–2.69	16
Ni	0.35–5.06	30
Pb	0.007–3.8	3
V	0.009–1.77	27
W	0.1–180	3.7
Zn	0.27–27	23

^a After GERM (<http://earthref.org>).

^b After Gaillardet J., Viers J., Dupré B. 2003. *Surface and Ground Water, Weathering and Soils, Treatise on Geochemistry*, Elsevier, Oxford, 5:225–227.

Wastewater used on farmland is generally a source of several trace elements. Therefore, the possibility of contamination should limit this method of wastewater disposal because of the accumulation of hazardous amounts of trace metals in surface soil (Figure 2.3).

Several threshold limits are established for concentrations of trace elements in waters: drinking, irrigation, and coal mine (Kabata-Pendias and Mukherjee, 2007). The most crucial are health-related limits for potable waters.¹³⁵⁷ Limits for discharge waters are also of great importance for the total “geochem” balance in the environment.

IV SOIL

A SOIL CONTAMINATION

Soil is a very specific component of the biosphere because it is not only a geochemical sink for contaminants but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota. However, the most important role of soil is its productivity, which is basic for the survival of humans. Thus, maintenance of the ecological and agricultural functions of soil is the responsibility of mankind.

Two terms—*soil contamination* and *soil pollution*—have been defined differently in various publications. The definition given by Knox et al.¹³⁶⁷ refers to soil contamination as soil whose chemical state deviates from the normal composition but does not have a detrimental effect on organisms. Pollution occurs when an element or a substance is present in greater than natural (background) concentrations as a result of human activity and has a net detrimental effect on the environment and

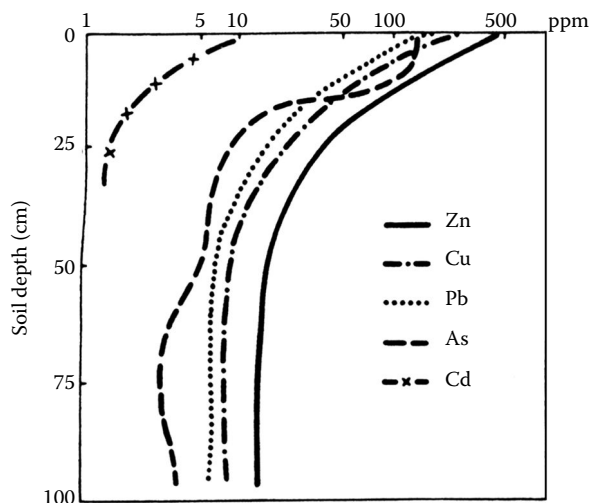


FIGURE 2.3 Vertical distribution of Zn, Cu, Pb, and Cd in a profile of the soil sludged during a period of 15 years and the distribution of As in light soil polluted by a metalliferous mine. (Data from de Haan, F. A. M., *Wastewater Renovation and Reuse*, Marcel Dekker, New York, 283, 1977; Kitagishi, K. and Yamane, I., eds., *Heavy Metal Pollution in Soils of Japan*, Japan Science Society Press, Tokyo, 302, 1981.)

its components. Thus, from a plant, animal, and human health perspective, soils are not considered polluted unless a threshold concentration exists that begins to affect biological processes.

Metal pollution of soils is as old as man's ability to smelt and process ores, and has been documented, especially in Greenland's snow and ice.¹²⁴¹ The metal emission, mainly of Pb, is now observed on local, regional, and global scales, especially throughout Europe. This phenomenon goes back as far as the Bronze Age (2500 BP). Any age of cultural development has left metal pollution of the environment, stored mainly in soil, sediment, and ice. Ernst¹²⁹⁴ comprehensively reviewed ancient metal contamination from the Bronze Age to Roman times. There is evidence that the long-range transport of trace elements and contamination, especially of organic surface soil horizons in natural remote regions, is not a recent phenomenon (Steinnes and Friedland, 2006).

Trace elements originating from various sources may finally reach the surface soil, and their further fate depends on soil chemical and physical properties and especially on their speciation. Although the chemistry of soil contaminants has recently been the subject of many studies, our knowledge of the behavior of polluting trace elements is far from complete. The persistence of contaminants in soil is much longer than in other compartments of the biosphere, and contamination of soil, especially by trace metals, appears to be virtually permanent. Metals accumulated in soils are depleted slowly by leaching, plant uptake, erosion, or deflation. The first half-life of trace metals, as calculated by Iimura et al.³³⁶ for soils in lysimetric conditions, varies greatly (in years): Zn, 70–510; Cd, 13–1100; Cu, 310–1500; and Pb, 740–5900. From the compilation of data given by Bowen,⁹⁴ the following residence time of trace elements in soils of temperate climate can be estimated: for Cd, 75–380 years; for Hg, 500–1000 years; and for Ag, Cu, Ni, Pb, Se, and Zn, 1000–3000 years. In soils of tropical rainforests, the rate of leaching of some elements is much shorter and is calculated at about 40 years. All similar estimations have clearly indicated that the complete removal of metallic contaminants from soils is nearly impossible.

The input–output balance of metals in soils shows that trace metal concentrations in surface soil are likely to increase on a global scale, with growing industrial and agricultural activities. The balance of trace metals in rural soils vary greatly, depending on farm kinds (Table 2.6).

Crop farms may generate higher inputs, than animal farms, of trace metals to soils. However, a great variation between farm types is also observed and this depends mostly on crop and soil types.

TABLE 2.6**Trace Metal Balance (g/ha/year) for Livestock Farms in Some EU Countries (Selected Data from the AROMIS Data Base^a)**

Country	Farm	Cd	Cr	Cu	Ni	Pb	Zn
Czech Republic	Pigs	1.2	11	30	4	17	220
Finland	Dairy	0.5	15	117	20	12	593
France	Pigs	6.7	53	924	-3.9	8.8	1784
	Dairy	5.7	—	1037	—	13	2594
Germany	Pigs	0.5	41	371	21	58	1276
	Dairy	1.8	32	908	21	36	798
Norway	Dairy	0.1	215	-138	32	1.3	-131
United Kingdom	Dairy	3.0	19	100	6	55	354

^a After Eckel H., Roth U., Döhler H., et al. (eds) 2005. Assessment and reduction of heavy metal input into agro-ecosystems. Final Rep. Eu-Concerted Action AROMIS, KTBL-Schrift, Darmstadt.

Balances for trace metals in crop-farm soils are presented in the AROMIS database (Eckel et al., 2005) as follows (in g/ha/year):

- Cd: from 0.3, Denmark to 4.4, France
- Cr: from 14, Denmark to 100, France
- Cu: from 35, France to 347, Germany
- Ni: from 3.3, Denmark to 33, France
- Pb: from 1.3 Norway to 139, France
- Zn: from 115, Germany to 838, France

Urban soil pollution has recently become a subject of many studies. The annual increment of trace metals caused by dust fallout in Tokyo is estimated for Cd to be 0.05 mg/kg and for Pb and Mn to be about 0.5 mg/kg.³⁹⁵ The background values for trace metals in residential soils from Southeastern Missouri (the United States) were exceeded by 2–31%, being the lowest for Mn and the highest for Pb (Ikem et al., 2008). De Mique et al.^{1417a} based on the investigations of pollution in Oslo (Norway) and Madrid (Spain), have distinguished so-called “urban” pollutants: Ba, Cd, Pb, Sb, Ti, Zn, and to a smaller extent Cu. Results of several other investigations have indicated, however, that the pollution of cities is specific and varies with local conditions; for example, in Warsaw (Poland), the relative increase is noticed for Li, Ni, Zn, Cr, Pb, Ba, Sr, and Fe (Figure 2.4). During the 20 years (from 1977 to 1997), a moderate increase in Pb, Cd, and Cu, but not in Zn, was noticed in soils along the streets of Warsaw: Cd from 6.0 to 10.0, Cu from 36 to 45, and Pb from 150 to 190 (average, mg/kg).¹²⁶⁸ An extreme increase of traffic intensity was also observed in Warsaw at that time. Jankiewicz and Adamczyk (2007) reported that in the city of Łódź (Poland), impact of the coal power plant on trace metals in soils was not observed, however the main source of the pollution was traffic; the highest contents (mg/kg) in urban soil were: Co, 43; Cr, 61; Pb, 262; and Zn 1390. In Novosibirsk (Russia), relative increases were observed for As, Br, Cd, Cu, Hg, Mo, Pb, Zn, and Zr,¹³⁴⁰ and in Minsk (Belorussia) for Cd, Pb, and Cu.¹⁴⁵² A high increase of trace metal contents in soils of central Saint Petersburg, as compared with soils of surrounding areas, are reported by Umfitseva and Terekhina (2005) as follows: (in mg/kg), for downtown and surrounding soils, respectively: Cd, 1.5–0.2; Cu, 120–18; Cr, 92–13; Pb, 223–19; and Zn, 774–43. In Siena (Italy), Ba and Pb were the most increased metals, and Ba has been proposed as a tracer for vehicle emissions, in place of Pb.¹⁴²³

The accumulation of trace metals in soil contaminated by automobile service varies with the weather. It is pronounced especially in the case of Hg, the content of which in soil during rainy season (4.8 mg/kg) is higher than during dry season (2.7 mg/kg) (Onweremadu et al., 2007).

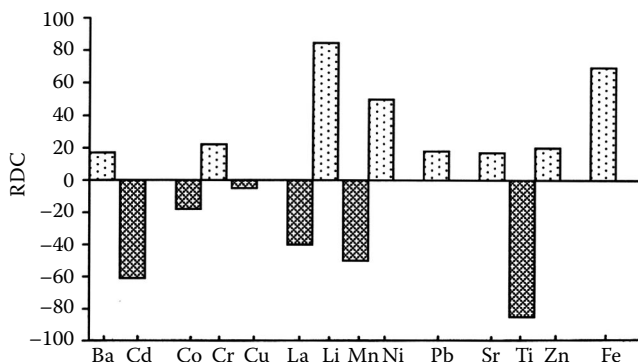


FIGURE 2.4 Variation in the content of trace elements in dandelion (*Taraxacum officinale* Web.) leaves collected in Warsaw (1995) and presented as RDC values. RDC, Relative Deviation to Constant; $RDC = \{[AM - RF]/RF\} \times 100$; AM—metal content of sample; RF—reference content of metal. (Modified from Kabata-Pendias, A. and Krakowiak, A., *Proc. 5th Int. Conf. Transport, Fate and Effects of Silver in the Environ.*, Argentum, Madison, WI, 145, 1998.)

However, Zn and Pb are the most commonly enriched metals in the soils of many cities.¹³⁶¹ Madrid et al. (2006) analyzed contents of five trace metals in surface soils of urban parks from six European cities. The lowest concentrations of all metals were in Aveiro (Portugal), (median value in mg/kg): Cr, 10; Cu, 16; Ni, 9; Pb, 20; and Zn, 49. Park soils from Glasgow (U.K.) contained the highest amounts of: Cu, 88; and Pb, 279, and soils from Torino (Italy) had the highest concentrations of: Cr, 177; Ni, 195; and Pb, 279. Urban soils of Talcahuano (Chile) contain metals at a slightly elevated range, (mg/kg): Cr, 37.8; Ni, 22.6; Pb, 35.2; and Zn, 333.0 (Tume et al., 2008). Birke and Rauch calculated the geogenic and anthropogenic fractions of the total accumulated metals in soils of Berlin area.¹²²⁷ The relative (in % of total) anthropogenic accumulation is highest for Zn, Hg, Cu, and Cd (60–80%), medium for Ni, Pb, and Sn (50–60%), and low for Ag and Cr (20–30%). The lowest anthropogenic origin, 1%, is given for Zn. Chemical fractionation of trace metals in urban soils (Guangzhou, China) indicated that only Cd was associated with HOAc extractable fraction, whereas Mn and Pb were concentrated mainly in reducible fraction, and Cu, Fe, Ni, and Zn were increased in residual fraction (Lu et al., 2007).

The regional contamination of soils, as reported most commonly, occurs mainly in industrial regions and within centers of large settlements where factories, motor vehicles, and municipal wastes are the most important sources of trace metals. Due to the long-distance aerial transport of trace pollutants, especially those that form volatile compounds (e.g., As, Se, Sb, and Hg), it has become difficult to estimate the natural background values for some trace elements in soils. Several methods were developed to calculate background (pristine) contents of trace elements in soils. There is great demand for such data as reference values because entirely natural contents of trace elements do not currently exist. In general, these methods are based either on statistical calculations or on the relation of trace element to various soil parameters and geologic factors. Some of the best-known methods are described below:

1. GB—*Geochemical Baseline* values are calculated as concentration ranges bracketed by the GM/GD^2 to the $GM \times GD^2$. These encompass the central 95% of observed contents (after Tidball and Ebens¹⁵¹⁸).
2. IGD—*Index of Geochemical Distribution* is calculated as $GM + 2GD$. TM soil status: (a) pristine: $MC/IGD < 1$, and (b) contaminated: $MC/IGD > 1$ (after Kabata-Pendias¹³⁵²).
3. IGL—*Index of Geochemical Load* is calculated versus geochemical background: $\log_2 MC/BC \times 1.5$. TM soil status: (a) pristine: $IGL < 3$, and (b) contaminated: $IGL > 3$ (after Müller¹⁴³⁸).

4. IPD—*Index of Pedogenic Distribution* is based on the comparison of TM distributions in soils: (a) vertical, (b) lateral, and (c) typological (after Baize¹²¹²).
5. PEF—*Pedochemical Enrichment Factor* is calculated versus Clarke's values of mother rocks and normalized to Al contents: $[MC/Al_s]: [CC/Al_r]$, TM soil status: (a) pristine: $PEF < 1$, and (b) contaminated: $PEF > 1$ (after Kabata-Pendias^{1349,1350}).
6. FSP—*Factor of Soil Parameters* is based on the selection of the most significant soil factor that controls TM contents. The content of clay granulometric soil fraction (0.02 mm) was established as a major soil factor for the evaluation of TM background concentrations within soil textural groups (after Kabata-Pendias and Krakowiak¹³⁵⁵).
7. SCV—*Spatial Concentration Variability* is based on geochemical baseline values and allows establishment of observed limits of values at a given distance from the source of pollution (after Gough and Crock¹³¹²).
8. GIS and MA—*Geographical Information System and Multivariate Analyses*, and also other statistical methods, are used to differentiate anthropogenic from natural anomalies in soils and plant roots (after Zhang and Selinus^{1572, 1573}).

Abbreviations: TM = trace metals, GM = geometric mean, GD = geometric deviation, MC = measured value, BC = geochemical background content of a given element, CC = Clarke's value, SCF = soil clay fraction, Al_s = Al content of soil, and Al_r = Al content of rock.

Very useful are PEF and FSP indices. The first is calculated in relation to trace element contents of mother rocks against so-called "stable" elements (e.g., Al, Ti) (Figure 2.5), and the second is based on the relation between clay soil fraction and trace element contents. Also, the interpretation of routine survey data based on isoline plots has been used for classifying soil contamination.¹²⁷²

The estimation of critical time when a metal in soil will reach its ecologically critical concentration is a subject of recent studies. As Pačes¹⁴⁴⁷ calculated for a given agricultural catchment in the Czech Republic, the steady state concentrations of Cu and Zn in the soils will never overshoot the critical load, while As, Cd, and Pb will reach the norms set for the soils after 4.5, 61, and 980 years, respectively.

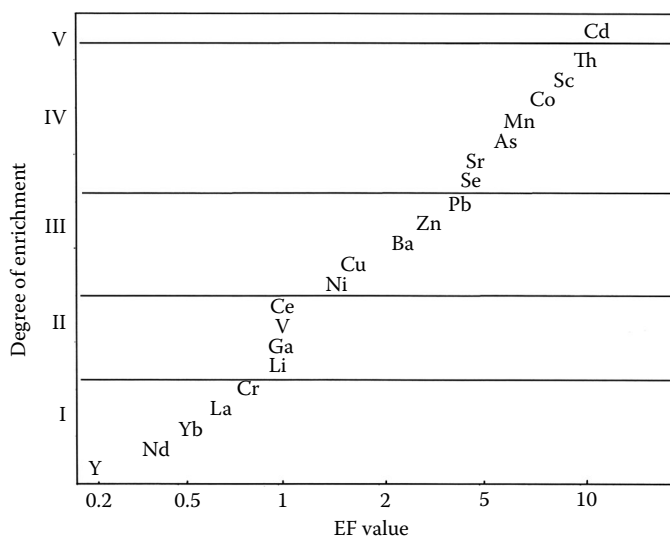


FIGURE 2.5 Enrichment factor (EF) values for trace elements in surface sandy soils of Poland as compared with mean concentrations (Clarke) in sandstones, and normalized to Al contents. Degree of EF: I—decrease, II—relative stability, III—slight increase, IV—moderate increase, V—strong increase. (Adapted from Kabata-Pendias, A., *Trace Subst. Environ. Health*, 25, 53, 1991.)

Elevated concentrations of trace elements can also be of lithogenic (geogenic) origin. This was reported by Čurlík and Forgač¹²⁶⁷ for some alluvial soils, by Baize¹²¹⁴ for soils derived from limestones, and by Skiba¹⁴⁹⁸ for soil of southern Spitsbergen (Sorrkap Land) derived from mica shales.

In addition to aerial sources of trace pollutants, fertilizers, pesticides, and all sewage-derived materials have added to the trace element pool in soils (Table 2.7). The mobilization of trace metals from smelter and mine spoil by transport with seepage waters or by windblown dust may also be an important source of soil contamination in some industrial regions. Goodroad,²⁷³ Piotrowska and Wiacek,⁶²⁰ and Stenstrom and Vahter^{755a} reported that long-term use of inorganic phosphate fertilizers adds substantially to the natural levels of Cd, F, and U in soils, while other elements such as As, Cr, Pb, and V do not increase significantly. There are reported increased contents of trace metals (Cu, Zn, Cd, Pb, Cr, As, and Hg) in vegetable fields (bare and greenhouse) as compared with grain crop field, due to a different pattern of use (Huang and Jin, 2008). Local, but serious is the problem of contamination by metals, especially with Pb, in soils from military shooting areas. Robinson et al. (2008) reported that over 400 t of Pb enters soils from military shooting ranges in Switzerland. Metals were concentrated in rhizospheric soils at the following amounts (geometric mean, mg/kg): Pb, 10,171; Sb, 5067; Cu, 4125; and Ni, 917. Wetland soils in Uganda (Lake Victoria basin) contain elevated amounts of metals (mg/kg): Zn, 387.5; Pb, 171.5; Cu, 51.2; and Ni, 21.3, due to industrial and municipal waste disposal (Nabulo et al., 2008). Agricultural soils from the vicinity of the abandoned Au–Ag mine in Korea contain increased levels of As and Hg, up to (mg/kg) 626 and 4.9, respectively (Lim et al., 2008).

Contamination of surroundings of old abandoned metal mines and effects of sewage sludge applications on soil composition are especially of great environmental concern and have been the subject of many studies and much legislation. Advisory standards and guidelines for safe addition of trace elements in sewage sludge to land is still in the stages of experiment and negotiation; however, several authors have given threshold values for the maximum addition of trace elements in one dose and over a period of time (Table 2.8). Despite some diversity of opinion, there is general agreement, especially regarding the maximum concentrations of trace metals in soils. It should be emphasized, however, that all the allowable limits need to be related not only to the given plant–soil system, but also to ratios between single elements as well as to their total burden in soil.

Franklin et al. (2005) concluded that analyzed fertilizers and fertilizer materials applied for 50 years should not present any health risk associated with food chain transfer to humans. However, some materials used for soil amendments may result in doubling the concentration of selected elements in 20 years of application. As Gupta and Gupta (2005) concluded, a long-term agronomic damage can result from excessive applications of certain elements. Thus, farmers require information on the length of time that trace elements/micronutrients remain effective in soil. There are observations that excessive application of fertilizers and manure affect increased concentrations of trace metals, and especially of Cd in the wheat-maize rotations (Ju et al., 2007). Dach and Starmans (2005) analyzed factors responsible for a difference in trace metals status in the Polish and Dutch agricultural soils and concluded that the main source of metals, mainly Cu and Zn, is the manure application. Feedstuffs contain about 5–10 mg Cu/kg and 30–40 mg Zn/kg, what resulted in increased levels of these metals in manure (Table 3.14).

Trace element contents in phosphate fertilizers, as reported by US EPA (1999) are (mg/kg, mean and range):

- As–11.3; 0.5–20.0
- Cd–65; 0.15–250
- Cr–173.2; 63–896
- Cu–56.6; 0.2–1170
- Ni–27.5; 0.5–151

TABLE 2.7
Trace Elements in Fertilizers, Sewage Sludge, and Fly Ash^a (mg/kg)

Element	P20 ^b	SS ^c	PM ^d	Fly Ash ^e
Antimony, Sb	0.20	2.4	0.16	3.8
Arsenic, As	9.1	2–26	1.3	60
Barium, Ba	123	150–4000	72	398
Beryllium, Be	0.14	<0.6–13	0.13	11
Bismuth, Bi	0.06	0.73	0.013	—
Boron, B	7.6	15–1000	28	509
Bromine, Br	—	20–165	0.25	1.3
Cadmium, Cd	0.11	2–1500	0.25	1.3
Cerium, Ce	1027	20–1027	7.1	112
Cesium, Cs	0.32	0.63	0.14	16
Chromium, Cr	12	20–40,600	11	118
Cobalt, Co	5	2–260	1.1	29
Copper, Cu	109	50–3300	113	72
Dysprosium, Dy	35	1.7	0.33	9.5
Erbium, Er	9.1	1	0.18	—
Europium, Eu	25	0.3	0.11	—
Gadolinium, Gd	87	2	0.77	—
Gallium, Ga	0.69	3.5	0.45	11
Germanium, Ge	0.16	4.3	0.05	6.6
Gold, Au	0.003	0.8	0.002	—
Hafnium, Hf	0.48	1.3	0.45	—
Holmium, Ho	0.024	0.4	0.07	—
Indium, In	<0.005	0.15	<0.01	—
Iridium, Ir	0.001	<0.4	<0.0001	—
Lanthanum, La	422	16	4.1	56.5
Lead, Pb	9.1	33–3000	2	52
Lithium, Li	3.6	4.3	1.5	235
Lutetium, Lu	0.56	0.2	0.02	0.7
Manganese, Mn	307	60–9300	250	325
Mercury, Hg	0.024	0.1–55	0.02	52
Molybdenum, Mo	0.56	1–40	6.8	14.6
Neodymium, Nd	594	11.3	2.9	—
Nickel, Ni	11	16–5300	6.1	87.9
Niobium, Nb	0.83	4.5	0.34	—
Palladium, Pd	<0.001	0.16	0.01	—
Platinum, Pt	0.003	<0.04	<0.001	—
Praseodymium, Pr	136	2.8	0.8	—
Rhenium, Re	0.0007	<0.04	0.0008	—
Rhodium, Rh	0.002	0.04	<0.001	—
Rubidium, Rb	6.8	15	224	106
Ruthenium, Ru	0.003	0.08	<0.001	—
Samarium, Sm	113	1.8	0.49	—
Scandium, Sc	3.5	0.5–7	0.27	—
Selenium, Se	0.032	1.3–10	0.89	1.6
Silver, Ag	<0.0005	7.4	0.018	—
Strontium, Sr	1720	40–360	76	720
Tantalum, Ta	0.011	0.94	0.003	1.5
Tellurium, Te	<0.0005	0.16	0.006	—
Terbium, Tb	9.8	0.34	0.066	1.6
Thallium, Tl	0.11	0.15	0.026	1.4
Thorium, Th	48	2.4	0.35	22.1
Thulium, Tm	0.89	0.2	0.025	—

TABLE 2.7 (continued)
Trace Elements in Fertilizers, Sewage Sludge, and Fly Ash^a (mg/kg)

Element	P20 ^b	SS ^c	PM ^d	Fly Ash ^e
Tin, Sn	0.34	22–700	1.3	8.9
Titanium, Ti	259	1800	57	—
Tungsten, W	0.023	7.9	0.11	4.5
Uranium, U	9.6	10	2.2	22.9
Vanadium, V	17	18	6.1	208
Ytterbium, Yb	5	1.1	0.16	4.8
Yttrium, Y	114	11	2.1	43.8
Zinc, Zn	54	550–49,000	680	221
Zirconium, Zr	21	5–90	2.6	194

^a Adapted from Eriksson J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm. Unless otherwise indicated.

^b Phosphate fertilizers, element concentrations expressed in mg/kg P.

^c Sewage sludges, data from Harmsen, K. and de Haan, F. A. M., *Neth. J. Agric. Sci.*, 28, 40, 1980; Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 300, 1979 (Po); Kloke, A., *Gesunde Pflanz.*, 32, 261, 1980a; Senesi, N. and Polemio, M., *Fert. Res.*, 2, 289, 1981; Smith, I. C. and Carson, B. L., *Trace Metals in the Environment*, Vol. 6, Ann Arbor Scientific Publications, Ann Arbor, MI, 1202, 1981; Stenström, T. and Vahter, M., *Ambio*, 3, 91, 1974; Trudinger, P. A. and Swaine, D. J., eds., *Biogeochemical Cycling of Mineral-Forming Elements*, Elsevier, Amsterdam, 612, 1979.

^d Solid pig manure, element concentrations expressed in mg/kg P.

^e After Llorens J.F., Fernandez J.L., Querol X. 2000. *Environ. Geol.* 40:409–446.

TABLE 2.8
Limit Values for Trace Elements in Fertilizers and Maximum Application Rates

Element	MAC for Fertilizer Products ^a	MAC for Fertilizers ^b	Maximum Application Rate ^c
As	75	25	0.018
Cd	20	1.5	0.113
Cr	—	600	1.650
Cu	—	300	0.327
Hg	5	1.0	<0.001
Mo	20	1500	—
Ni	180	100	0.095
Pb	500	100	0.282
V	—	—	0.452
Zn	1850	1500	0.971

^a Canadian MAC values (mg/kg) in fertilizer products. After US EPA. 1999. Background report on fertilizer use, contamination and regulations, EPA-747-R-98-003. Office of Pollution Prevention and Toxics, Washington, DC.

^b MAC values (mg/kg) established in Finland for fertilizers used for agricultural soils (Dahl et al., 2008).

^c Maximum annual application rate (kg/ha/year) established by US EPA (1999).

- Pb–12.2; 1–200
- V–216; 48.7–721
- Zn–240.2; 31.3–1150

Mean concentrations of trace metals in these fertilizers do not exit proposed MAC values (Table 2.8). US EPA (1999) estimated what fertilizer products will double the U.S. soil background levels of trace metals in 45 years. These calculations indicated that all fertilizers applied at both average and maximum rates will double Cd soil levels. Also, most fertilizers will double As and Pb levels. Increase of Cu and Zn in soils is associated mainly with NPK fertilizers. However, organic/biosolids fertilizers and home fertilizer products also may be a serious source of trace metals.

Phosphate fertilizers are considered to be a serious source of trace metals in agricultural soils. Input of metal depends on the TM:P ratio in the rock phosphate and on the annual rate of P-fertilization. Nziguheba and Smolders (2008) calculated TM input with P-fertilizers to soils of several European countries, within the range as follows (g/ha/year):

- Cd: 0.1 (Finland)–3.1 (Portugal)
- Ni: 0.7 (Sweden)–6.2 (Portugal)
- Pb: 0.3 (Belgium)–2.5 (Ireland)
- Zn: 11.1 (Denmark)–134.7 (Finland)
- Cr: 1.5 (Finland)–42.3 (Portugal)
- As: 1.1 (Sweden)–2.4 (Finland)

Variable use of agricultural soils has an impact on trace elements concentrations. Increasing acidification during recent decades has led to ecological disruption observed in many European countries. A steady increase of hydrogen ions in top soils, resulting mainly from emitted sulfur and nitrogen dioxides leads to an imbalance of all nutrients, and further, to destruction of natural buffering properties of soils. A common effect of these changes is an increased mobility of all cations. A high rate of trace metal mobility in soils affects the increase of both bioavailability and leaching down soil profiles into water systems. Loamy neutral soils may accumulate a higher amount of trace elements with much less environmental risk. However, a general chemical imbalance of such soils usually results in decreased biological activity, in decreased or increased pH, and, as a further consequence, in degradation of organic and mineral sorption complexes.

Contamination of agricultural and forest soils has already become relatively common and is likely to continue. Noticeable, also, is the fact that most often soils become contaminated by several metallic pollutants that are accompanied quite frequently by acid rains (mainly SO₂, NO_x, and HF). Such an association of pollutants in soil greatly complicates their impact on the environment. Trace elements and other inorganic and organic pollutants are known to accumulate in surface soils as a result of both contamination from point sources (industrial, urban, and agricultural) and from long-range aerial transport. However, soils and other surficial sediments cannot act as permanent storage for immobile trace elements. The remobilization processes will again transfer these elements into biogeochemical cycles, and as a consequence, will disturb the intricate interrelationship of the flow of elements and energy in the soil-plant-animal system.

The state of our knowledge about the impact of trace inorganic pollutants on soil ecological variables is relatively broad. There is not enough data, however, to attempt to set up definite values for criteria needed to protect soils against the long-term effects of trace element pollution. Some preliminary values have, however, been proposed as guidelines for primary hazard assessments. These guidelines for threshold levels, “trigger concentrations,” of trace elements, and particularly trace metals, will differ from place to place to meet the variable ecological conditions of each region or country. These should, however, be based on similar standard methods and experimental

procedures for the measurement of the content of each element. A number of observed ecological standards are often used to assess the significance of trace metal levels in soils. These include:

NOEC—No Observed Ecological Consequences
HNOAEC—Highest No Observed Adverse Effect Concentration
LKE—Lowest Known Effect (or Level)
LOEC—Lowest Observed Effect Concentration
PAA—Permissible Annual Application
MAC—Maximum Allowable Concentration
MAL—Maximum Allowable Loading
MPL—Maximum Permissible Loading
MCA—Maximum Cumulative Amount
RMCL—Recommended Maximum Contaminant Levels
ATL—Action Trigger Level (the concentration above which remedial measures and treatments are necessary)
ELD—Ecosystem Lethal Dose
LOAEC—Lowest Observed Adverse Effect Concentration

Approaches to setting limits for trace elements, MAC, are based on fundamental criteria such as: (1) transfer of trace elements (mainly metals) to various organisms and to man; (2) assessment of the likely harmful effects; (3) estimation of two threshold values, LOAEC and HNOAEC; and (4) evaluation of metal balance (input–output) of metals. Recently, the concept of critical loads (CLs) has been widely discussed in order to develop the precautionary assessment of risk due to the future inputs. In these models multiple scales for CLs, variable mechanisms and different receptors of potential concern should be considered (Lofts et al., 2007).

Values given in the Third Edition compared to those cited now (Table 2.9) indicate a tendency for more liberal limits, especially for metals of concern in agriculture practice and food production: Cd, Cr, Cu, Hg, Ni, Pb, and Zn. The proposed increase for Cd-MAC for 6–20 times is a subject of special concern.¹⁴⁰⁸

In several soils, the threshold levels have already been exceeded, either in gardens and orchards or in other locations, by contamination from industrial emissions or heavy and repeated applications of sewage sludges in urban areas and soils near highways. A high trace metal content of sludges is the most important hindrance to their use in agriculture. Although Purves⁶³⁴ reported that in practice the concern with using sludges commonly is only their phytotoxicity due to excesses of Zn, Cu, and Ni, their content of Cd in particular, and of Pb and Hg, should be of concern as serious health risks. As Andersson and Nilsson²⁵ have observed, long-term use of sewage sludge increased the levels of Zn, Cu, Ni, Cr, Pb, Cd, and Hg in the soils. Of these elements, however, only Zn, Cu, Ni, and Cd increased in cereal grains, and Zn, Cu, Cr, and Pb increased in cereal straw. Chaney¹²⁷ and Sikora et al.⁷²⁶ recommended higher doses of sewage sludges because of the relatively low availability of trace metals in plants. Recently, the attention has been focused on wood ashes (from increasing wood burning) spread in forests, as a serious source of metals, especially Pb, Cd, and Pb (Reimann et al., 2008).

The immobilization of trace metals by sewage sludge is apparently due to the fixation of metals mainly in forms (operational) of oxides (Figure 2.6). In other soil conditions, however, the effect of sewage sludge can be different, and some trace metals can be mobilized as, for example, complexes with small organic molecules. As Crompton¹²⁶⁴ stated, we can only poorly understand what bio-transformations from inorganic metals to organometallic compounds can occur when metal-contaminated sewage sludge is disposed of as fertilizer on agricultural land. The presence of inorganic metals in sewage sludge creates a potential for the formation of organometallic compounds by biosynthetic processes. Thus, an understanding of all factors influencing the phase distribution of metals in soils is a prerequisite to estimating the critical loads of metals and their effect on soil

TABLE 2.9
Ranges of Maximum Allowable Concentrations (MAC)
or Trigger Action Value (TAV) for Trace Metals in
Agricultural Soils (mg/kg)

Metal	MAC ^a	TAV ^b
Ag	—	2–40
As	15–20	10–65
Ba	—	400–600
Be	10	10–300
Cd	1–5	2–20
Co	20–50	30–100
Cr _{total}	50–200	50–450
Cr ⁶⁺	—	3–25
Cu	60–150	60–500
Hg	0.5–5	1.5–10
Mo	4–10	5–20
Ni	20–60	75–150
Pb	20–300	50–300
Sb	10	10–20
Se	—	3–10
Sn	—	35–50
V	150	100–340
Zn	100–300	200–1500

^a Values reported most commonly in the literature, compiled from Kabata-Pendias A., Sadurski W. 2004. *Elements and their compounds in the environment*, 2 ed. 79–99, Wiley-VCH, Weinheim; Chen Z.-S. 1999. Selecting indicators to evaluate soil quality. Accessed April 1999: <http://www.fft.agnet.org>

^b Values proposed in some European countries, compiled from various reports, documents, and internet data.

organisms. Beckett et al.⁵⁹ concluded that in addition to the commonly monitored levels of Cu, Ni, Zn, Cd, Cr, and Pb during the disposal of sewage sludge on farm land, it may be necessary to monitor levels of Ag, Ba, Co, Sn, As, and Hg and also possibly Mo, Bi, Mn, and Sb, until their likely accumulations in surface soil can be shown to be harmless. Now it is evident that several other elements, such as lanthanides, actinides, and PMGs should be monitored in soils heavily fertilized and/or under high doses of sewage sludge.

Although trace metal-contaminated soils have gained much attention, the excess of other trace elements, such as B, Br, F, and Se can also be, in some regions, of environmental concern. In many cases, increased concentrations of these elements in surface soils are associated with soil salinity affected by irrigation/drainage practices and processes. Elevated concentrations of these elements may also be related to composition of parent material and to the impact of the chemical industry, coal combustion, and leaching from waste landfills.

The behavior and, especially, the phytoavailability of cations in soils are governed predominantly by their speciation and by several soil properties. The speciation and localization of metallic contaminants in soils are related to their chemical forms at the time of impactation. Aerial particles transporting trace metals are most common in mineral forms of oxides, silicates, carbonates, sulfates, and sulfides, and when they originated from coal combustion, the glassy structure predominates. Trace metal species entering soils with sewage sludge differ based upon the source and the treatment of wastes. The forms associated with sesquioxides and with compounds bound to

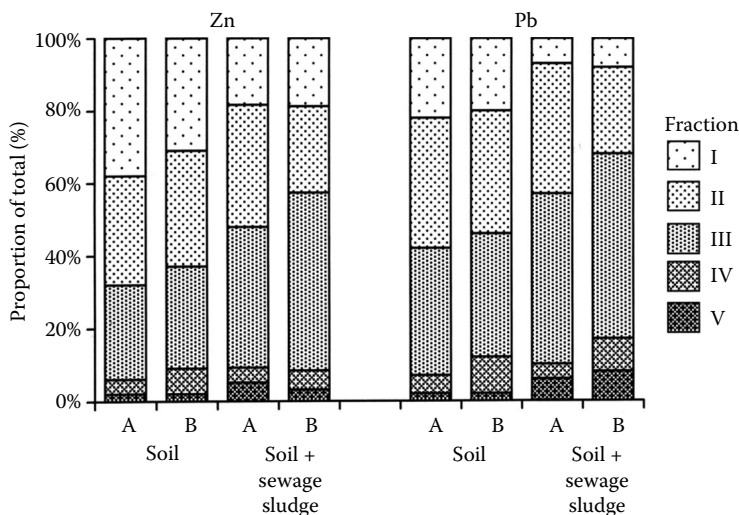


FIGURE 2.6 Impact of sewage sludge on fractionation of Zn and Pb in medium sandy soil (A), and loamy soil (B). Fractionation according to Tessier et al. (Data from Tessier, A., Campbell, P. G. C., and Bisson, M., *Analyt. Chem.*, 51, 844, 1979): I—exchangeable, II—carbonate, III—oxide, IV—organic, V—residual. (Modified from Mánko, P., *Mobility and Phytotoxicity of Heavy Metals in Sulfur-Contaminated Soil*, Ph.D. thesis, IUNG, Puławy, 1999, 70 (Po).)

organic residual fractions usually predominate in sludge of municipal origin. When wastes are mixed with some industrial effluents, however, the speciation of metals greatly differs based upon the discharged forms from factories.

Effects of excessive levels of trace metals on soil properties depend on complex reactions between the trace cations and other components of all soil phases—solid, liquid, and gaseous. These reactions have been broadly studied in recent years, and several principles, mechanisms, and models were established and proposed by the authors.^{954,1153,1154} The chemical forms governing the mobility and phytoavailability of trace metals and residence times of pollutants in soil layers are the main subjects of mechanistic modeling and calculations. The mobile fraction of trace metals behaves like bivalent cations in soil phases and is controlled by dynamic equilibria between solid and liquid phases. However, the complexity of all possible reactions in natural heterogeneous soil systems needs more data for an appropriate prediction of ecological consequences of the soil pollution with trace metals. The fate of these metals in soils depends upon many soil processes that can be generalized as follows:

- Dissolution
- Sorption
- Complexation
- Migration
- Precipitation
- Occlusion
- Diffusion (into minerals)
- Binding by organic substances
- Absorption and sorption by microbiota
- Volatilization

All these processes are governed by several soil properties, of which soil pH and redox potential are known to be the most important parameters. Thus, the solubility of trace metals is often shown as a function of pH affected by the amount and kind of organic matter (Figure 2.7). Also other soil

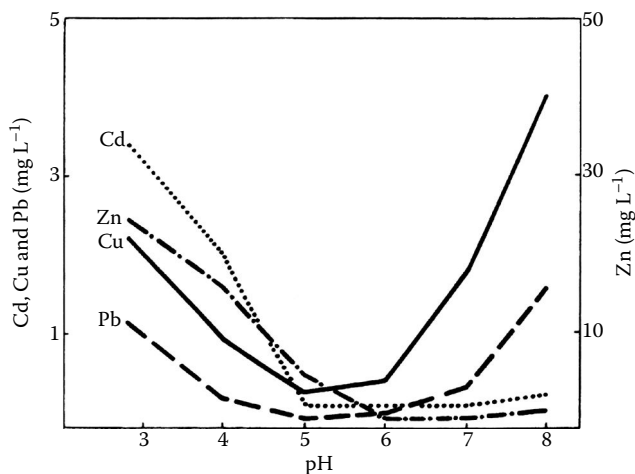


FIGURE 2.7 Concentrations of trace metals in equilibrium solutions of sandy gleyic podzol. (From Brümmer, G. W. and Hermes, U., *Effects of Accumulation of Air Pollutants in Forest Ecosystems*, D. Reidel, Dordrecht, 233, 1983. With permission.)

factors, such as CEC, carbonates, Fe and Mn hydrous oxides, clay minerals, and fine granulometric fractions are known to play significant roles in the behavior of trace elements. Frequent association of trace element pollution with the acid deposition (mainly SO_2 and NO_x) greatly complicates overall ecological disturbance created by the chemical degradation of soils.

Soil contaminated with trace metals can produce apparently normal crops that may be unsafe for human or animal consumption. Klope³⁹⁸ calculated that if the content of Hg, Cd, and Pb in the soil is not higher than the threshold values (Table 2.8), it can be expected that the contents of these metals in human diets will not exceed tolerable weekly intakes established by FAO/WHO. Therefore, safe use of sewage sludge must be assessed on the basis of a safe addition of trace metals into soils.

Permissible levels of trace elements, particularly trace metals, used on farmland can be calculated based on several factors. Thus, permissible levels of trace elements in surface soils differ highly based on local conditions. For example, the estimates based on geochemical principles and general hygienic limitations proposed by Goncharuk and Sidorenko¹⁰¹¹ and Niezbizhskaya and Saet¹¹⁰⁰ are much lower than those calculated for the protection of vegetation, given by El-Bassam and Tietjen,²⁰⁶ Kitagishi and Yamane,³⁹⁵ and Klope.³⁹⁸ It is most important, however, to evaluate acceptable application rates in relation to:

- Initial trace element content of soil
- Total amount of one element added
- Cumulative total load of trace metals
- Trace metal dose limitation
- Equivalency of trace element toxicity to plants
- Threshold values of trace element concentrations in soils
- Relative ratios between interacting elements
- Soil characteristics (e.g., pH, free carbonates, organic matter, clay content, and moisture)
- Input–output balance
- Plant sensitivity

In addition to general ecological effects, criteria should take into account damaging effects on crops, injury to animals—particularly the hazards associated with the ingestion of soil during

grazing—and possible accumulation effects that may occur in the food chain (e.g., geophagia). The possible contamination of human food is an especially urgent problem. To ensure safe quality of the food chain products, it is useful to standardize the allowable loadings of contaminants (MAL) to agricultural land.

Values for any critical concentration or loading of trace elements that can be established at the present time should be regarded as tentative and approximate assessments that may be changed with improvements in the database and understanding the significance of the presence of particular elements in particular soils, farming practices, or ecosystems. There is a real need for critical examination of the crucial questions concerning the standards that should be used to establish the criteria for “safe” limits for trace element contents of soils. Several proposals show a general agreement for most individual elements (Tables 2.8 and 2.9), but ultimate accepted values should take into account possible interactions between different trace elements and between trace elements and other components of soils. Agreement on criteria based on the measurements of the amounts of “available” elements present further problems because of the difficulty in deciding if “availability” should be measured in biological or chemical terms, and the exact way in which either can be measured.

The highest reported (compiled from Kabata-Pendias and Mukherjee, 2007) contents (in mg/kg) of some trace metals in soils contaminated from industrial sources in selected countries are as follows: As—2500 in China; Cd—1500 in the United States; Co—300 in China; Cu—3700 in Canada; Hg—100 in China; Pb—13,000 in the United States; Mo—100 in China; Ni 26,000 in Canada; and Zn—80,000 in the United States.

There is a growing concern about radionuclide contamination. Nuclear power generation has been utilized since the mid-1950s and accidental leakages in the surroundings of the nuclear installations were reported. The first widespread contamination by radionuclides was due to the explosion at Chernobyl (presently in Ukraine) in April 1986. Radionuclide contamination affected some European countries and several other parts of the world.

Becker-Heidmann and Scharpense (1990) reported that most important radioactive isotopes released by the Chernobyl accident were as follows:

- Short half-life time (days): ^{141}Ce , ^{132}Te , ^{133}Xe , ^{131}I , ^{99}Mo , ^{95}Zr , and ^{89}Sr
- Longer half-life time (years): ^{134}Cs , ^{85}Kr , ^{137}Cs , ^{103}Ru , and ^{90}Sr
- Long half-life time (hundreds of years): $^{238-240}\text{Pu}$, and ^{241}Am

The fallout of Chernobyl's isotopes varied greatly and the nonhomogenous distribution is partly associated with the wet precipitation (rainfall) during that period. The behavior of isotopes in soil depends on several soil properties, and on the specific behavior of each radionuclide. The distribution, fate, and phytoavailability of ^{137}Cs (half-life 30 years) have been investigated most frequently (Sheppard, 2003).

The highest radioactive contamination of surface soils of Poland, after the Chernobyl explosion, has been observed in the southwestern part of the country. The concentrations of ^{137}Cs in soils of those regions were at the range 5–13 kBq/m². During the period 1988–2001 the country average concentration of this isotope diminished from about 4.6 to 3.2 kBq/m² (Biernacka et al., 2004).

B SOIL REMEDIATION

As Kobabayashi et al.⁴⁰⁵ reported, some of the first actions for soil remediation were in Japan (in 60th year of the twentieth century), where an excess of soil Cd was removed by repeated treatment with EDTA solution and lime (the Cd content of the surface soil decreased from 27.9 to 14.4 mg/kg). Nowadays, a number of methods have been developed and used at field-scale, based on main technologies: (1) biological, (2) chemical, (3) physical, and (4) thermal/electrical. There are many programs and organizations, both at national and international levels, for hazardous

waste cleanup and sustainable land management, and information is easily available from web portal sites.

The remediation of soils refers to practices of either removing contaminants or converting them into to less mobile species; that is, into less bioavailable forms. The selection of a method is generally based on the nature of the contaminants, the soil type, and the characteristics of the contaminated site. Also remediation costs and regulations of the country should be involved in remediation projects (Alloway¹²⁰², Cunningham and Berti, 2000). A virtual explosion of various articles, reports, and books on soil remediation has been recently observed. Methods for remediating metal-polluted soils have been widely investigated and discussed (e.g., Sparks, 1995; Adriano et al., 1998; Knox et al., 2000; Iskandar, 2001; Pierzynski et al., 2005; Kumpiene et al., 2005, 2008). The remediation of soils and sites contaminated with radionuclides is of special concern. Several techniques, *in situ* and non *in situ* are applied to cleanup soils contaminated with trace metals. Owing to the complexity of soils and the presence of multiple contaminants, only a few of these techniques have been applied successfully in practice and some of them are quite costly. Most commonly used remediation technologies (*in situ* and non *in situ* methods) are:

- Leaching/washing/flushing—soil with water or surfactant (a surface active substance), not very commonly practiced, limited due to the need for large quantities of water, results depend strongly on physical soil parameters.
- Solidification/stabilization/immobilization—soil amendments with materials having a high capacity to bind metals in possible slightly mobile fractions and/or immobilize by keeping a neutral soil pH, for effectiveness required site-specific data, relatively low cost.
- Biodegradation—substances containing trace metals are decomposed due to microbial degradation, trace pollutants are mobilized and washed-out, long-term effects, practiced in specific sites.
- Phytoremediation—the phytoextraction techniques provide an adequate method under reasonable yield of plants that hyperaccumulate metals. It is promising in practice and of relatively low cost.
- Vitrification—pollutants are immobilized with an electric current, seldom used, very costly.
- Isolation/containment—minimizing downward migration of pollutants by installing subsurface barriers: for example, clay layer, organo-clay layer, plastic liner.
- Encapsulation—covering small sites with a layer of material of a low permeability (e.g., clay) to prevent water percolation and wind blow of dust.
- Immobilization of trace metals, for example, Fe/Mn oxides, which adsorb or occlude several trace metals, phosphoric compounds which decrease the mobility of most metals, and by several other substrates (e.g., clay minerals, Ca-carbonates, zeolites).
- Removal—the contaminated soil is exposed to chemical extraction and/or thermal treatment to remove volatile elements or compounds, and to other leaching or immobilizing processes, high costs.
- Excavation—the contaminated soil is removed and disposed elsewhere (e.g., in prepared landfills), high cost and possible problem with groundwater contamination.
- Coprecipitation by steel shots—containing mainly Fe oxides are effective in the immobilization of trace metal excess.
- Chemical reduction/oxidation.

Recent research (Engineered nanoparticles) has been developed based on Fe-NP, often coated with catalyst such as Pd and Pt, and effective especially in the groundwater remediation (Cundy, 2007). Fawzy (2008) investigated the efficiency of different mineral substrates to reduce the mobility of Cu and Zn, and reported that the most effective were treatments with Ca-carbonate, zeolite, and Mn/Fe oxides.

The problem of concern in soil remediation actions is the cost. Phytoremediation techniques are likely to be less costly than those based on conventional technologies. At present, an urgent requirement for phytoextraction is to increase the yield of plants that hyperaccumulate metals from soils and to develop adequate technologies for the utilization of plant materials.

Agricultural practices also have been applied to soil remediation. Most commonly, the uptake of metals by plants is diminished by keeping a neutral soil pH and by amendments with materials having a high capacity to bind metals in slightly mobile fractions. These are mainly: lime, phosphate fertilizers, zeolites, montmorillonite clays, OM/SOM, and biosolids. Al-montmorillonite reveals higher binding properties for Zn than for Cd.¹²¹¹ Liming is a very common practice to prevent their phytoavailability. However, effects of liming are a decreased mobility of other cation micronutrients. This has been clearly demonstrated by Siebielec and Chaney (2006), who found Mn deficiency in plants grown in soil limed to remediate Ni-phytotoxicity. Several authors (Knox et al., 2000; Basta et al., 2001; Adriano et al., 2004; Naidu et al., 2006; Kumpiene et al., 2008) have described effects of natural attenuation, using agricultural chemicals (e.g., lime, phosphate compounds, secondary minerals, Fe oxides, organic compounds) in reducing mobility and thus phytoavailability of metals. In each case of metal fixed by binding materials, the question arises as to the persistence of this immobilization, under what soil conditions, and in what time frame could it turn into a mobilizing effect.

Trace metal mobility in soils is known to be related to land use. Usually, metals in forest soils are more easily mobilized (e.g., bioavailable and leached) than metals in agricultural soils. This is directly related to the higher acidity of soils and to a higher presence of low-molecular-weight organic substances in forest soils than in arable ones. This phenomenon will be an environmental concern in the future due to programs of forestation of poor agricultural quality soils, especially in Europe.

A new method recently presented by Mench et al.¹⁴¹³ is based on the affinity of Fe and Mn oxides (or sulfates) to adsorb and occlude several trace elements from the ambient solution. Application of steel shots containing mainly Fe (over 90%) and oxides of other metals in negligible amounts (below 1%) resulted in immobilization of considerable amounts of trace metals in soil. Steel shots affect the uptake of As, Zn, Cu, Ni, and Pb by plants. The effect in Cd immobilization is apparently less successful.¹⁴¹⁴ Iron grit (zerovalent Fe) is proposed to be used for the stabilization of Cr, Cu, and As. This technique is especially effective in the fixation of As (Kumpiene et al., 2006).

Some experiments using earthworms to clean polluted soils were also conducted.¹⁴⁸⁶ Effects of this method vary with the specific conditions, and some elements are observed to be more easily taken up by earthworms (e.g., Cd and I) than others (Mn and Cs). The role of metal-resistant bacteria in soils has also been considered. Such bacteria can make plants more tolerant to metal pollution sites.¹³⁸⁷

C PHYTOREMEDIATION

At present, there is an extraordinary interest in bioextraction methods using phytoremediation, phytomelioration, and phytomining.^{1198,1266,1409} It is necessary to emphasize that restoring the soil's original properties may never be achieved, especially using technical methods. However, good restoration of soil properties can give good results when using some of the best technology for a given kind of soil and for the type and concentration of the contaminants.

Phytoremediation is an environmental cleanup strategy in which plants and their root-bound microbial community are used to absorb and remove trace elements in the contaminated soil and to translocate them to plant tissues (Robinson et al., 2003). Phytoremediation using plants that hyperaccumulate trace metals, especially when transgenic plant species can be used, seem very promising. Some plants (e.g., *Pergularia tomentosa*) from Saudi Arabia may accumulate very high amounts of elements (in mg/kg): As, 12.7; Cd, 76.7; Cu, 333; Pb, 89; and Zn, 720.6.

The problem of concern in soil remediation actions is the cost. Phytoremediation techniques are likely to be less costly than those based on conventional technology. However, as McGrath¹⁴¹⁰ stated,

full costs of plant-based techniques will not be known until mature technology is offered and applied. At present, the real demand for phytoextraction techniques is to increase the yield of plants that hyperaccumulate metals and increase the mobility of metals in soils. The most common plants tested recently for phytoremediation have been listed by Felix et al.¹²⁹⁸: *Alyssum murale*, *Thlaspi caerulescens*, *Nicotiana tabacum*, *Zea mays*, *Brassica juncea*, and *Salix viminalis*. The ability of several agricultural crop plant species, such as mustard, radish, turnip, rape, and amaranth, to accumulate higher amounts of some metals (Cd, Cr, Cu, Ni, and Zn) has been investigated as well.¹⁴⁹² Glass (2008) presented a versatile technology with many potential applications for the phytoremediation. He estimated that the world markets for phytoremediation in 1999 was \$34–58 million and predicted a great increase through 2024.

Plants that are able to take up metals above established background concentrations and more than other species from the same soils are called *hyperaccumulators*. These are mainly populations of species found in soils rich in metals either due to geochemical parameters or due to pollution. Hyperaccumulators usually have low biomass because they use more energy in the mechanisms necessary to adapt to the high metal concentrations in the tissues. Plants that highly accumulate metals are promising in phytoremediation programs.

The phytoremediation/phytoextraction techniques provide an adequate method under reasonable yield of plants that hyperaccumulate metals. It may be promising in practice and may be at relatively low cost, however, but needs development of technology. In this process, plants act as bio-pumps to remove contaminants and water from growth media. These processes can be divided into three following sections:

- Phytostabilization—binding of trace metals (metalloids) in an aerobic environment in the root zone.
- Phytoextraction—increased uptake of trace metals, mainly by hyperaccumulating plants, process that should be continued for several seasons to obtain an effect.
- Phytoextraction enhanced by chelation (e.g., addition of EDTA, APCAs etc.).
- Phytofiltration/rhizofiltration—absorption of metals (metalloids) in root tissues due to chelation and surface absorption from both soil and groundwater.

Recently, several articles have been published on this topic (Baker et al., 1994; Chaney et al., 1999; Cunningham and Berti, 2000; McGrath et al., 2001; Wenzel et al., 2003; Prasad, 2004; Evangelou et al., 2007). Hyperaccumulators are plants and/or genotypes that accumulate metals much above common concentrations. At present there are about 400 species that are known as hyperaccumulator plants (Robinson et al., 2003). Greger (1999) showed, based on the literature review, that hyperaccumulators may contain trace metals in leaves above the following levels (in mg/kg):

- 100—Cd;
- 1000—Co, Cu, Ni, Pb;
- 10,000—Mn, Zn.

Various wild plants species are known as hyperaccumulators, depending on growth conditions and contaminant. Most commonly *Alyssum*, *Thlaspi*, and *Astragalus* species are proposed for the phytoextraction of Ni, Zn, and Se, respectively. These plants, however, usually give a low yield and this limits their effectiveness. Thus, a number of cereal crops, such as wheat, rice, rye, oats, barley, corn, and sorghum, have been proposed recently to be used for phytoremediation as they can tolerate relatively high concentrations of metals.

The application of phytoremediation procedures for the cleanup of highly contaminated soils has been widely discussed (Shtangeeva, 2006). Calculated amounts of trace elements that are removed with plant yield are relatively small. Even accumulator plants withdraw, mainly from topsoils, about 10% of Cd, the most readily available metal (Kabata-Pendias, 1994). The utilization of crops enriched

in metals is a serious problem that has to be always included in the application of any phytoremediation methods. Such biomass could be used for the production of ethanol (bio-fuels) and straw (of corn and cereals) and can be burnt for the production of heat and electricity. Any yield of biomass that contains elevated amounts of metals is a hazardous waste which needs specific technologies to be utilized for the production of heat and energy or other secondary products. The ash from biomass power plants containing metals (e.g., Zn and Cd) can be recycled to recover these metals. The phytovolatilization method can be applied for elements which are highly volatile, such as Se, As, and Hg.

V PLANTS

The significant role of plants in both cycling of trace elements and contaminating the food chain has been well illustrated for various ecosystems and published in numerous papers. Plants can accumulate trace elements, especially trace metals, in or on their tissues due to their great ability to adapt to variable chemical properties of the environment. Thus, plants are intermediate reservoirs through which trace elements from soils, and partly from waters and air, move to man and animals. As Tiffin⁷⁸⁹ has concluded, plants may be passive receptors of trace elements (fallout interception or root adsorption), but they also exert control over uptake or rejection of some elements by appropriate physiological reactions.

Using plant chemical status for geochemical prospecting is a very old practice in the exploration of metal ores. Some of the first scientists who provided geochemical background information for plant-based prospecting were Vernadsky¹⁵³² and Warren.⁸⁴⁸ Recent reviews of biogeochemical prospecting are presented by Dobrovolsky¹²⁸⁰ and Kovalevsky.¹³⁷² The response of plants to the chemistry of the environment is controlled by several external and biochemical factors. Nevertheless, the chemical analysis of plants is a promising tool to study chemical properties and changes in the biosphere.

Plants reveal a variable and sometimes specific ability to absorb trace elements from soil. The ratio of an element in plants to its concentration in soil, a so-called Biological Absorption Coefficient (BAC), is widely used for comparing different plants. Three general uptake characteristics can be distinguished in plants: accumulation, indication, and exclusion. To a large extent, this depends on the specific ability of plants. A huge difference in metal uptake between plant species, and also between genotypes of a species, has been demonstrated in many studies. Comprehensive information on this is given in recent publications edited by Brooks,¹²⁴⁴ and by Prasad and Hagemeyer.^{1459,1460} Some plants reveal a special capability to accumulate a specific element. For example, ladder brake (*Pteris vittata* L.), a terrestrial fern, can contain large amounts of As, up to 23,000 mg/kg (Ma et al., 2001). The unique properties of Chinese brake fern has great importance in the clearing of As-contaminated soils by the phytoremediation process. The laboratory study conducted by Tu et al. (2002) indicated that this plant might take up to 7230 mg As/kg within 20 weeks. Tu and Ma (2003) reported that the addition of phosphates is an important strategy in improving the removal of As from contaminated soils by brake fern. Some plants (e.g., *Pergulara tomentosa*) grown in Saudi Arabia may accumulate high amounts of elements (in mg/kg): Zn—720.6; Cd—76.7; Cu—333; Pb—89; and Zn—720.6 (Al-Faraj and Al-Wabel, 2007).

The biota reveals the potential to develop a resistance upon anthropogenic loads of trace elements to ecosystems. However, the biodiversity and biological activity of polluted ecosystems are very poor, as commonly observed in the vicinity of industrial plants and especially metal smelters. Several authors have observed that the yield of various crops can be decreased due to metallic pollution (Figure 2.8). The generalized effects of metal concentrations in nutrient solution on yield and metal content of plants are shown in Figure 2.9.

The most significant toxic effect of the excess of trace elements, according to Prasad and Hagemeyer¹⁴⁶⁰ are, as follows:

- Changes in permeability of cell membranes—Ag, Au, Br, Cd, Cu, F, Hg, I, Pb, and U.
- Reactions of thiol group with cations—Ag, Hg, and Pb.

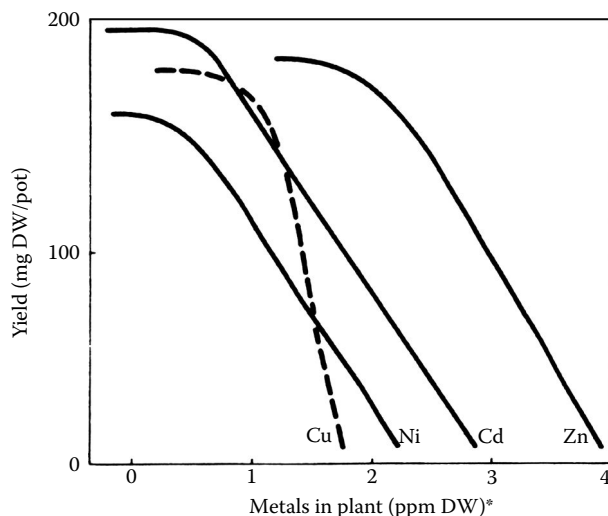


FIGURE 2.8 Response of young barley plants to trace metal concentrations in their tissues. Asterisk indicates concentration of metals is given in powers of 10. (Modified from Beckett, P. H. T. et al. *Water Pollut. Control*, 78, 419, 1979.)

- Competition for sites with essential metabolites—As, Sb, Se, Te, W, and F.
- Affinity for reactions with phosphates (ADP and ATP) and several TMs, including Cs, Li, Rb, Y, lanthanides and several other metals.
- Replacement of sites for essential ions (mainly major elements)—Cs, Li, Rb, Se, and Sr.
- Occupation of site for essential groups such as phosphate and nitrate—compounds of As, B, Br, F, Se, Te, and W.

One of the basic environmental problems relates to the quantities of accumulated trace elements in plant parts used as food. However, special attention should also be given to their forms/species within plant tissues. Trace cations in plants occur mainly in organic complexes. Common chelating agents are organic acids (i.e., carboxylic, amino, mercaptic, mugineic, phytic),

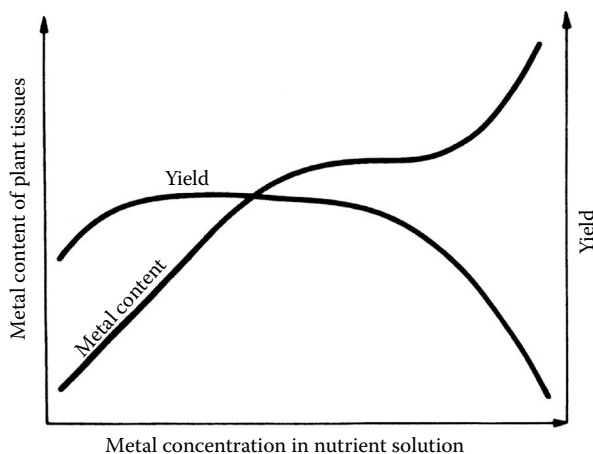


FIGURE 2.9 Generalized effects of trace metal concentrations in nutrient solution on yield and metal content of plants.

proteins, polysaccharides, lignins, pectins, DNA, metallothioneins, phytoferritins, and so on. Inorganic ligands like Cl, F, and sulfate are also complexants for trace metals. Plants are able to synthesize various metallo-complexes like methylmercury, organoarsenic, selenomethionine, and so on (Shaumlöffel et al., 2004; Chassaigne et al., 2001; Dauchy et al., 1994).

The chemical quality of plant food is a matter of public concern and is of primary importance in the program of consumer and health protection. Over the last decade, several expert committees, especially under various joint international commissions, have been collaborating in programs on the health hazard associated with the exposure to excess of trace elements in food chain. Several international commissions collaborate in various programs to protect humans against excess of trace elements in plant food, and in particular against Cd and Pb, for which the maximum levels and provisional intakes have been established (Kabata-Pendias and Mukherjee, 2007).

The study of the chemistry of soils and plants in relation to the incidence of geographically distributed diseases is the basis for the discipline of medical geochemistry. It has been initiated by Låg in 1980¹³⁸⁵ and has been recently developed by Selinus et al. (2005) and Catherine et al. (2003).

Each case of plant pollution is unique and should be studied for a specific environment. There is an increasing awareness that results of studies based on simulation-type systems cannot be related to those in a natural system. This fact is supported by de Vries and Tiller,⁸³¹ who reported a much lower absorption of trace metals by lettuce and onions grown in a market garden soil than by those grown under greenhouse and miniplot conditions. Trace pollutants entering plant tissues are active in metabolic processes, but can also be stored as inactive compounds in cells and on the membranes. In each case, however, they may affect the chemical composition of plants without causing easily visible injury.

A BIOMONITORING

Plants are good indicators and can serve as a measure of chemical status of a given site or area (see Chapter 5, VII. Bioindication). A basic characteristic of a good bioindicator are summarized by Witting¹⁵⁴⁶ as follows:

- Suitable accumulation of several or selected elements
- Tolerant and no sensitivity to the accumulated element
- Present in large amounts in the ecosystem under investigation
- Wide distribution in various environments
- No seasonal differences in availability and applicability
- Existence of a correlation between accumulation and input to the ecosystem

Plants also respond directly to the state of air. The tops of all plants are collectors for all air pollutants, and their chemical composition may be a good indicator for contaminated areas, when it is assessed against background values obtained for unpolluted vegetation. Mosses and lichens are known to be the most sensitive indicators of atmospheric pollution.^{1037,1135} Several other plants and plant organs are shown to be suitable indicators of pollution of soil and aquatic environments. Nettle is highly recommended by Ernst and Leloup^{990a} as a better biomonitor for metals, especially for Fe, than the other perennial herbs. A preferred phytoindicator is the common dandelion.^{1278,1356,1470} Compared to green plants, mushrooms can concentrate a large amount of several trace metals, and are also good indicators for environmental pollution.^{414,635,1008,1056} Mushrooms are known as the most sensitive accumulators of Se and Hg, for which concentrations are about a thousand times higher than in green plants. While Cd can be accumulated to high concentration ratios, Pb seems to be excluded from mushrooms. Cu and Zn levels are higher in mushrooms than in associated vascular plants, but their concentration ratios (against soil) are relatively low.^{1008,1045} Moss analyses, however, provide more suitable and reliable techniques for survey of atmospheric metal deposition.

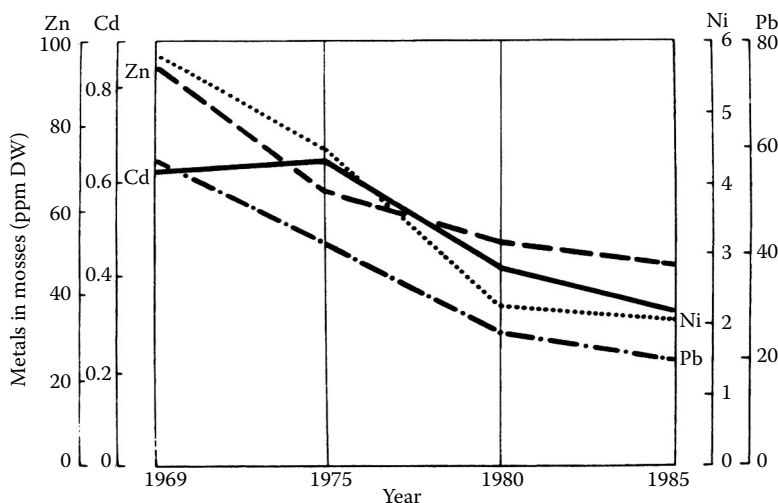


FIGURE 2.10 Trends in decreasing Zn, Cd, Ni, and Pb contents in moss species (*Hylocomium splendens* and *Pleurozium schreberi*) in the central part of Sweden during the decades 1960–1980. (From Rühling, A. et al. Survey of Atmospheric Heavy Metal Deposition in Nordic Countries in 1985, Report for Nordic Council of Ministers, Kobenhavn, 1987. With permission.)

The broad program of environmental monitoring in the Nordic countries has been based on the survey of metals in mosses. Trends observed by Rühling et al.¹¹³⁵ in decreasing metal contents of mosses during recent decades (1968–1985) indicate a reduced emission of Zn, Cd, Ni, and Pb (Figure 2.10).

Berries and mushrooms grown in forests are also good in bioassays of pollution. Plants grown in the vicinity of the Ni–Cu smelter complex at Monchegorsk, Kola Peninsula, Russia, show a linear correlation between the metal content of fruits and their concentration in soil.¹²¹⁶ Berries (*Vaccinium vitis-ideae* and *Empetrum hermaphroditum*) had up to about 30 mg/kg Cu and 25 to 40 mg/kg Ni on soils with 3000 mg/kg of both metals, whereas the most sensitive mushrooms (*Russula vesca*) contained Ni and Cu at levels of 125 and 133 mg/kg, respectively. Mushrooms from Japanese forests are also broadly used in bioassays of trace element pollution.¹⁵⁶⁴

A broad study on the distribution of trace metals in the forest ecosystem near the city of Serpukhov (120 km southeast of Moscow) was carried out by Zolotareva et al.¹⁵⁷⁸ The authors observed that Mn is likely to concentrate in leaves, whereas all other metals are distributed variably among the parts of trees and herbs. The ability of plants to uptake elements, expressed as the transfer factor, is similar for trees, grasses, and mosses; the highest values were always for Mn and Zn, and the lowest for Fe and Pb.

Several recent research projects have been carried out on the environmental impact of the past anthropogenic activities. It has been shown that rainwater-fed bogs (ombotrophic *Sphagnum* bogs) can be used as archives of atmospheric dust deposition.¹³⁶³ As Shotyk¹⁴⁸⁸ reported, As, Cu, Pb, and Zn are more abundant in surface and near-surface peat layers compared to deeper parts of the profile. The maximum enrichment factors are approximately 5 times for Cu, 15 times for As, and 30 times for Pb, Sb, and Zn. Variations in the Ti concentrations of peat correspond to changes in soil dust inputs due to soil wind erosion and agricultural development, whereas Pb is an indicator of past mining and smelting activities. The increase in Pb contents in Europe dates back to Roman times, but the highest rates of increase in the enrichment factor are for the Middle Ages and for modern times in central Europe.¹³⁶³ More than 99.9% each of Cu, Pb, and Zn is bound to an organic phase, either the solid phase or the solution in peat bog pores. This explains a chemical mechanism by which metal migration in the peat profiles may be significantly retarded.¹⁴⁸⁷

Peat-bog records of trace metal accumulation are considered a measure of total net deposition. As Nikolishin et al.¹¹⁰¹ described, the long-distance aerial distribution of Pb and Zn resulted in an increase in their concentrations in sphagnum peat in the remote area of Siberia during the last half-century 1910–1970, from below 30 to above 100 mg/kg AW.

Tree rings have recently been used to examine past environments. Each ring represents 1 year of growth, thereby preserving evidence of past conditions. Geochemists studied the radial distribution of Zn and Mo in cottonwood from the Summiville mine areas in Colorado and found increased levels of Cu, Zn, and Mo in tree rings after mining activity.¹³⁶⁴ The interpretation of the chemistry of tree rings, however, is complicated by several processes affecting the incorporation of elements into wood tissue. The spatial distribution of water transport, damage to tree roots, and cation binding capacity in the xylem are some factors that govern tree-ring chemistry. Therefore, additional information on the sites and ways of trace metal deposition in woods is needed for a correct dendroanalytical interpretation of element distribution. As Brackhagen et al.¹²⁴² observed, radial distribution patterns of Cd and Zn in stems of Scots pine trees did not correspond with the known timing of pollution inputs to respective forest stands. However, concentrations of Cd and Zn in stem wood were higher in trees growing on contaminated plots.

There are several other conditions required for suitable bioindication and biomonitoring methods. These conditions are related to standardized sampling and analytical methods, comparing results with other monitoring methods, and possible retrospective and long-time investigation periods.

Dandelion is reported quite frequently as a useful environmental indicator, since this plant fulfills most of the listed demands.^{1278,1356,1470} Rule (1994) also confirmed the suitability of dandelion as a versatile phytomonitor. An evaluation of metal pollution in selected regions of Poland using dandelion is presented in Table 2.10. Dandelion leaves grown in the industrial region (Region SW) contain

TABLE 2.10
Metals^a in Leaves of Dandelion Grown in Different Regions of Poland (mg/kg)

Metal	Whole Country N = 780	All Regions N = 240	Region SW N = 60	Region SE N = 70	Region NW N = 60	Region NE N = 50
Cd	0.5 220	0.6 0	1.2 50	0.6 0	0.5 220	0.4 250
Cu	9.4 227	9.4 222	13.4 10	10 220	8.4 242	7 271
Cr	0.8 25	0.8 25	0.7 14	1.3 53	0.7 14	0.4 250
Mn	60 0	65 7	74 18	103 41	69 13	42 218
Ni	3.4 50	1.3 253	4.2 52	6.4 68	3.1 35	1.9 25
Pb	1.1 281	1.2 266	3 33	1 2100	1 2100	0.5 2300
Zn	45 0	50 10	72 37	67 32	35 228	40 212

Source: Data from Kabata-Pendias, A. and Krakowiak, A., *Proc. 5th Int. Conf. Transport, Fate and Effects of Silver in the Environ.*, Argentum, Madison, WI, 145, 1998.

^a Upper values for metals are Geometric Means and lower are RDB (Relative Deviation to Background) values, $RDB = \{[AM - 2 RF]/RF\} \times 100$.

RF—reference contents (mg/kg): Cd 0.6, Cr 0.6, Cu 12, Mn 60, Ni 2, Pb 2, Zn 45.

more trace metals than dandelion leaves from other areas. The RDB value identifies a very high relative deviation from background values of all metals in plants from industrial regions.

Soil microorganisms are considered good candidates for bioindication of soil metal pollution. However, Parkhurst et al.¹⁴⁴⁹ have described some problems with using a population of microorganisms or microbial activity as soil biomonitors. These include a large natural variation in population size and activity of microorganisms in soils and their sensitivity to all chemical and physical soil factors. Some examples, however, indicate that the bioassay could be used to assess the bioavailability and harmful effects of trace metals.¹⁴⁶² Screening for the presence of rhizobia can be a rapid method for the soil bioassay of toxic effects of trace metals and allows the determination of the bioavailable pool of metals in soils.^{1310,1332}

The inhibitory effect on soil bioactivity expressed as the soil respiration, differs considerably among trace metals but is always a function of metal contents. The general order of toxicity of metals to microorganisms can be presented as follows: $\text{Ag} > \text{Cu} > \text{Cd} > \text{Ni} > \text{Zn} > \text{Pb} > \text{Mn}$. Two metals, Cu and Zn applied as sulfates to the soil at concentrations up to 2000 mg/kg, affect soil microbiota: fungi (glucophilic, cellulose-decomposing, thermophilic, and thermotolerant), bacteria, and actinomycetes, generally causing reduction in their populations and in soil enzyme activities.¹³²⁵ Soil enzyme activity has been used as a sensitive indicator of the effect of trace metals on soils. Most soil enzymes are inhibited by metals; for example, at contents (in mg/kg) of: Cu, 900; Cr, 842; and As, 1124). The decrease of enzyme activity is in the following order (relative to control values): phosphatase, 70%; urease, 31%; sulfatase, 25%; and dehydrogenase, 17%.¹⁴⁶¹ Alkaline and acid phosphatases are reported to be most sensitive to excess of Cd, Co, and Zn.¹⁴⁴³

3 Soils and Soil Processes

I INTRODUCTION

A valid concept of the nature of soil must avoid the common error that soil is simply a mixture of unconsolidated material, resulting from the weathering processes of underlying rocks. Soil is a natural body, having both mineral and organic components in addition to physical, chemical, and biological properties. Soil properties, therefore, cannot be a simple reflection of the combined properties of all soil components.

Any classification of soils suffers from the disadvantage that it is impossible to relate it to the great complexities of soil genesis and properties. The terms used in defining the soils in different systems are seldom exactly equivalent. The definitions of soil units used in this book are adopted from the FAO/UN (2006). Short descriptions of the soil units are presented in [Table 3.1](#). The names of soils described in this book were taken from the original publications, translated, and the associated soil characteristics were fitted, insofar as possible, into the soil units of the FAO/UN.

The composition of soils is extremely diverse and although governed by many different factors, climatic conditions and parent material predominate most commonly. An approximation of soil composition is shown in [Figures 3.1](#) and [3.2](#). Soil is composed of three phases: (1) solid (mineral and organic), (2) liquid, and (3) gaseous, and it exhibits properties resulting from the physical and chemical equilibriums of these phases. Moreover, not only the chemical composition of the solid components of soil but also its mineral structure and the state of dispersion are important factors influencing soil properties.

Although trace elements are minor components of the solid soil phase, they play an important role in soil fertility. Knowledge of the association of trace elements with particular soil phases and their affinity to each soil constituent is the key to a better understanding of the principles governing their behavior in soils. The “normal concentrations” of trace elements in soils are of great interest as background values needed for any assessment of the degree of soil contamination.

Based on the large database of recent surveys on trace elements in soils, several mean values are presented for trace elements in worldwide soils ([Table 3.2](#)). The database allows the estimation of the concentration ranges and arithmetic means which are presented for several trace elements in the selected soil types ([Table 3.3](#)). These data give the approximate information on possible concentrations of trace elements in uncontaminated soils. The relationship between WRB soil units ([Table 3.1](#)) and selected trace metals is discussed for soils of Argentina (Roca et al., 2008). Increased accumulation of some trace metals in alluvial soils is often observed as effects of both flood–water transport and fine granulometric composition (Vodianizkii, 2008). The background contents of trace elements in soils, both uncontaminated and contaminated, seem to be log-normally distributed with much higher extremes in contaminated ones.

Some authors have emphasized a need to determine local baseline concentrations, because bedrocks highly influence natural contents of trace elements. There are several recent publications on the baseline levels of selected trace elements in soils of various regions, for example: Brazil (Melo et al., 2006), Italy (Sartori et al., 2004), Japan (Yamasaki et al., 2001), European Russia (Beznosikov et al., 2007), and Spain (Bech et al., 2008).

Background contents of trace elements in soils are governed by several factors among which geological and physico-chemical properties are of great importance. For example, concentrations of As, Cr, and Co in soils developed on the Fe-oolitic sandstone in Luxemburg are (mg/kg): 123, 126,

TABLE 3.1
Reference Soils Groups Established for the WRB^a by FAO/UN

Name of Soil Group	Code for Reference Soil Group	World Distribution ^b	U.S. Soil Group	Predominating Soil-Forming Factor ^c	Short Description of Soils
Acrisols	AC	7.97	Ultisols (part)	c	Strongly leached acid soils, on a variety of parent materials
Albeluvisols	AB	—	Glossaqualfs, etc.	b	Soils formed under coniferous forest, mainly from glacial till
Alisols	AL	—	Ultisols	c	Weathering products of basic parent materials
Andosols	AN	0.76	Andisols	a	Soils formed from volcanic glasses and ash, or other silicate-rich materials
Anthrosols	AT	—	Anthrosols (in Australia)	—	Soils formed under a predominant influence of man's activity
Arenosols	AR	10	Psamments	a	Soils formed from sand, in places calcerous
Calcisols	CL	—	Calcids	a	Soils formed from glacial till and other materials, with a petrocalcic horizon
Cambisols	CM	7	Inceptisols	a	Weathered from various parent material, enriched in illuvial clay and organic matter
Chernozems	CH	—	Mollisols	a, b	Soils formed mainly under prairie vegetation and from aeolian sediments
Cryosols	CR	13	Gelisols	a, b	Soils formed on glacial till and other residual material, associated with tundra vegetation
Durisols	DU	—	Durids	a	Soils formed on silicate-rich, mainly alluvial deposits, on sloping plains
Ferralsols	FR	8	Oxisols	c	Soils with sesquioxide-rich weathered material from basic rocks and siliceous deposits, mainly in under tropical climate
Fluvisols	FL	2.4	Fluvents, Fluvaquents	a	Soils formed from recent fluvial, lacustrine and marine
Gleysols	GL	4.7	Aqualfs, etc.	a, c	Wetland soils formed from various hydromorphic materials, mainly fluvial sediments
Gypsisols	GY	—	Gypsid	a	Soils formed from base-rich alluvial, colluvial or aeolian deposits
Histosols	HS	2	Histosols	b	Soils on incompletely decomposed plant remains, without admixture of sand, silt or clay
Kastanozems	KS	—	Ustolls, Xerolls	b	Dark brown soils rich in organic matter, often developed in loess
Leptosols	LP	—	Lithics, Entisols	a	Soils developed on slightly weathered rocks or on unconsolidated materials

TABLE 3.1 (continued)
Reference Soils Groups Established for the WRB^a by FAO/UN

Name of Soil Group	Code for Reference Soil Group	World Distribution ^b	U.S. Soil Group	Predominating Soil-Forming Factor ^c	Short Description of Soils
Lixisols	LX	—	Latosols, Alfisols	a	Soils developed on strongly weathered and leached finely texture materials
Luvisols	LV	7	Alfisols	c	Leached soils on a variety of unconsolidated materials; glacial till and aeolian or alluvial deposits
Nitisols	NT	—	Inceptisols, Oxisols	b, c	Finely textured soils on basic parent rocks, often with admixtures of volcanic ash
Phaeozems	PH	4	Udolls, Albolls	b	Dark soils rich in organic matter, mainly on glacial till or other unconsolidated materials
Planosols	PL	1	Albaqualfs, Albaquults	c	Soils slightly leached due to a slowly permeable horizon, mainly in subtropical regions
Plinthosols	PT	—	Plinthaquox, etc.	a	Soils rich in Fe (Mn), commonly formed from weathered basic rocks
Podzols	PZ	3.6	Spodosols	c	Soils, with illuviation horizon, developed from weathered siliceous rocks and various deposits.
Regosols	RG	10.1	Entisols	a	Soils developed from little altered, unconsolidated finely grained materials
Solonchaks	SC	2	Salids	c	Soils, often formed from unconsolidated deposits, with salt accumulation, in arid and semi-arid regions
Solonetz	SN	—	Natric groups	c	Soils with hydromorphic properties, rich in exchangeable Na and/or Mg, derived mainly from fine-textured sediments
Stagnosols	ST	—	Aqualfs, Aquults, etc.	c	Soils (similar to Luvisols), highly leached, formed on various unconsolidated materials
Technosols	TC	—	—	—	Soils formed under a predominant influence of man's activities
Umbrisols	UM	—	Entisols, Inceptisols	c	Soils with dark top horizon, developed from siliceous rocks, in mountainous, humid regions
Verisols	VR	2.4	Vertisols	a	Heavy clay soils (cracking soils), with a high proportion of swelling clays

^a WRB—World Reference Base for Soil Resources, after FAO/UN (2006).

^b The distribution in percent of the global land surface, as given by Dudal.¹⁹⁴

^c Factors: a, parent rock; b, vegetation; and c, pedogenic processes stimulated mainly by climate.

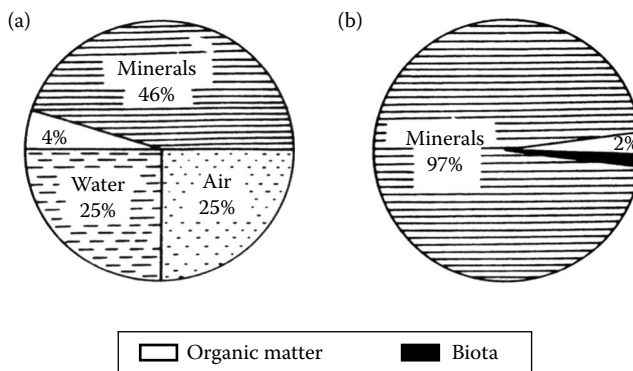


FIGURE 3.1 Approximate composition of a representative silty loam surface soil of vertisol soil unit (brown soil). (a) Volume percent of total soils; (b) weight percent of solid phase of soil.

and 33, respectively (Horckmans et al., 2005). Upper baseline values for selected elements in soils of Catalonia District in Spain are (mg/kg): Ba, 618; Cr, 120; Cu, 112; Ni, 119; Pb, 218; Sr, 129; V, 101; and Zn, 327, being higher for Pb and Zn than reported in the literature (Bech et al., 2005).

Gałaszka (2007a) reviewed geochemical background concepts and stated that these values are different for remote areas that are governed mainly by the geologic setting, and thus it should be assessed only at a local or regional scale.

II WEATHERING PROCESSES

Two stages are involved in the formation of soils from parent material. The first is the alteration of primary mineral constituents of the parent rocks by the physical and chemical processes of weathering. The second stage (pedogenesis) results in the formation of a soil profile from the weathered rock material, leading to the development of a mature zonal soil as the end point of the interacting processes. Weathering and pedogenic processes cannot be easily distinguished and separated because they may take place simultaneously at the same sites and most commonly they are closely interrelated. They will be discussed separately, however, in chapter subsections.

Weathering, the basic soil-forming process, has been extensively studied and reviewed as the complex interactions of the lithosphere, the atmosphere, and the hydrosphere that occur in the biosphere and that are powered by solar energy. Weathering can be chemically described as the processes of dissolution, hydration, hydrolysis, oxidation, reduction, and carbonatization. All of these processes are based on rules of enthalpy and entropy, and they lead to the formation of mineral and

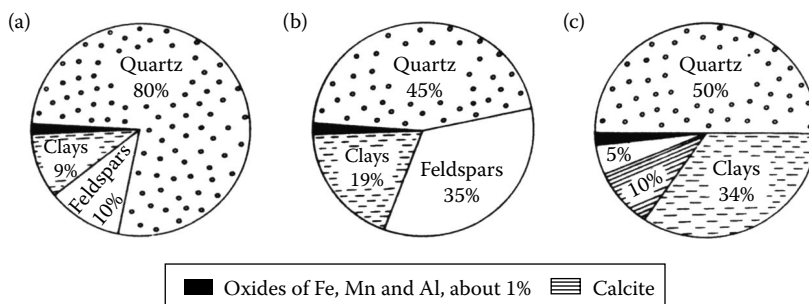


FIGURE 3.2 Approximate composition of mineral constituents of surface soils derived from different rocks in a temperate humid climate. (a) Podzol over sandstone; (b) Vertisol over granite; (c) Calcisol.

TABLE 3.2
Commonly Reported Mean Background Contents of Trace Elements in Continental Crust and Surface Soils (mg/kg)

Element	Crustal Average ^a	World-soil Average	A	B	C	D	E	F
Antimony, Sb	0.2	0.67	0.62	0.25	0.78	—	0.66	1.04
Arsenic, As	1.8	6.83	4.7	3.8	—	—	7.2	11.6
Barium, Ba	400	460	362	608	350	—	580	400
Beryllium, Be	3	1.34	1.9	1.3	1.4	—	0.92	2.0 ^b
Bismuth, Bi	0.2	0.42	0.7	0.16	0.33	—	—	0.5 ^b
Boron, B ^d	15	42	57 ^b	57 ^b	23 ^b	43 ^b	33	—
Bromine, Br	2	10	—	—	—	10.5	0.85	—
Cadmium, Cd	0.1	0.41	1.1	0.17	0.33	0.18	<0.01–41	0.28
Cerium, Ce	60	56.7	49	60	52	89	75	52.2
Cesium, Cs	3	5.06	8	1.7	5.4	4.6	—	5.58
Chlorine, Cl	640	300	380	—	—	—	—	—
Chromium, Cr	100	59.5	42	22	58	86	54	94.8
Cobalt, Co	10	11.3	6.9	7.1	18	17	9.1	10.4
Copper, Cu	55	38.9	14	17	48	109	25	17.3
Dysprosium, Dy	3	3.6	0.7	4.1	3.9	5.6	—	3.58
Erbium, Er	2.8	2.2	1.6	2.2	2.2	3.1	—	2.1
Europium, Eu	1.2	1.4	1.2	0.79	1.2	1.5	—	0.85
Fluorine, F	625	321	264	—	—	269	430	—
Gadolinium, Gd	5.4	3.9	2.2	3.4	4.2	5.5	—	4.2
Gallium, Ga	15	15.2	1.2	8.9	20	31	17	13
Germanium, Ge	1.5	2.0	1.2	1.9	—	1.9	1.2	—
Gold, Au	0.004	0.003	0.002	<0.005	—	0.002	—	—
Hafnium, Hf	3	6.4	3	7.6	2.5	12.7	—	6.1
Holmium, Ho	0.8	0.72	1.1	0.87	0.73	1	—	0.72
Indium, In	0.11	0.06	—	<0.04	0.09	0.11	—	0.05
Iodine, I	0.5	2.8	2.4	—	—	13	1.2	5.6
Iridium, Ir	0.00005	—	0.0009 ^c	<0.04	—	—	—	—
Lanthanum, La	30	27	26	33	23	34	37	26
Lead, Pb	15	27	25	18	24	22	19	32
Lithium, Li	20	21	28	17	13	24	24	—
Lutetium, Lu	0.3	0.37	0.34	0.39	0.31	0.52	—	0.31
Manganese, Mn	900	488	418	411	—	535	550	524
Mercury, Hg	0.07	0.07	0.1	0.043	—	0.053	0.09	0.061
Molybdenum, Mo	1.5	1.1	1.8	0.58	1.3	1.6	0.97	0.94
Neodymium, Nd	28	26	19	29	22	32	46	22
Nickel, Ni	20	29	18	13	26	25	19	37
Niobium, Nb	20	12	12	12	10	25	11	11
Osmium, Os	0.00005	—	0.0006 ^c	—	—	—	—	—
Palladium, Pd	0.004	0.02	0.0012 ^c	0.04	—	0.003	—	—
Platinum, Pt	0.004	0.02	0.0033 ^c	<0.04	—	0.002	—	—
Praseodymium, Pr	8.2	7	7.6	7.7	5.3	8.4	—	6.02
Rhenium, Re	0.0004	—	0.0004	<0.04	—	—	—	—
Rhodium, Rh	0.00006	—	0.0005 ^c	<0.04	—	—	—	—
Rubidium, Rb	90	68	50	116	70	18	67	87
Ruthenium, Ru	0.0001	—	0.0007 ^c	<0.04	—	—	—	—

continued

TABLE 3.2 (continued)
Commonly Reported Mean Background Contents of Trace Elements in Continental Crust and Surface Soils (mg/kg)

Element	Crustal Average ^a	World-soil Average	A	B	C	D	E	F
Samarium, Sm	4.7	4.6	3.1	4.5	4.4	6.7	—	4.3
Scandium, Sc	11	11.7	9.5	10	21	—	8.9	9.1
Selenium, Se	0.05	0.44	0.7	0.23	—	0.47	0.39	—
Silver, Ag	0.06	0.13	0.1	0.11	0.1	0.05	—	—
Strontium, Sr	375	175	147	163	190	—	240	130
Tantalum, Ta	2	1.39	1.1	1.1	1.7	2.3	—	0.76
Tellurium, Te	0.005	—	—	<0.08	—	—	—	0.04
Terbium, Tb	0.6	0.63	0.4	0.48	0.74	0.9	—	0.64
Thallium, Tl	0.5	0.5	0.6	0.23	0.49	0.36	—	0.82
Thorium, Th	7.2	9.2	8.2	8.1	9	11	9.4	9.2
Thulium, Tm	0.5	0.37	0.46	0.32	0.3	0.5	—	0.31
Tin, Sn	2.5	2.5	—	1.8	2.4	—	1.3	4.5
Titanium, Ti	4400	7038	—	3700	—	15,480	2900	6070
Tungsten, W	1.5	1.7	1.2	1.3	1.3	1.4	<0.17	<5.0 ^d
Uranium, U	2	3.0	3.7	4.4	1.9	2.9	2.7	2.4
Vanadium, V	135	129	60	69	180	320	80	68
Ytterbium, Yb	2.2	2.6	2.1	2.9	2.1	3.2	3.1	2.1
Yttrium, Y	33	23	12	27	21	27	25	23
Zinc, Zn	70	70	62	65	89	73	60	68.1
Zirconium, Zr	165	267	300	308	92	421	230	2.1

Note: Given are mean values for various soils of different countries: A—worldwide data after Kabata-Pendias and Pendias,¹³⁵⁷ B—agricultural soils of Sweden, after Eriksson (2001), C—agricultural soils of Japan, after Takeda et al. (2004), D—medians for soils of Parana State, Brazil, after Licht (2005), E—data for the U.S. soils, after Burt et al. (2003), and Shacklette and Boerngen,⁷⁰⁶ F—means for top soils of Europe, after FOREGS (2005).

^a Values are compiled from Mason and Moore (*vide* Hedrick, 1995) and Reimann and de Caritat (1998).

^b Median value.

^c Roadside top soil samples from ca 10 m distance from road in Austria (Fritsche and Meisel, 2004).

^d Values for B from various sources and countries, as follows: A, China; B, Israel; C, New Zealand; and D, Russia.

chemical components that are relatively stable and equilibrated in the particular soil environments. Biochemical weathering leads to the destruction of parent minerals and to the passing of elements from the minerals into solutions and suspensions.

Living organisms and their decomposition products play a significant role in weathering. Two types of compounds released by organic matter or organisms are believed to be particularly involved in weathering processes: carbon acid, formed from CO₂ released during decay of organic matter, and organic chelates. Stevenson¹¹⁵⁷ described that most cations released from rocks and minerals during weathering form soluble complexes with natural organic chelates. These processes are comprised of several stages from the first attack on insoluble mineral matter by simple organic chelates excreted by microorganisms to complete saturation of the chelating sites in organic matter, and to the incorporation of the elements into living tissues.

Greatly simplified, basic weathering processes can be characterized as follows:

- Dissolution: minerals are soluble in the aquatic phase
- Hydration: minerals increase their water content

TABLE 3.3
Ranges and Means^a of Total Concentrations of Trace Elements in Surface Soils^b Calculated on the World Scale (mg/kg)

Element	Podzols		Cambisols		Calcisols/Leptisols		Kastanozems/ Chernozems		Histosols	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
As	<0.1–30	4.4	1.3–27	8.4	—	—	1.9–23	8.5	<0.1–66.5	9.3
B	1–134	22	<1–128	40	1–210	40	11–92	45	4–100	25
Ba	20–1500	330	19–1500	520	150–1500	520	100–1000	520	10–700	175
Cd	0.01–2.7	0.37	0.08–1.61	0.45	0.38–0.84	0.62	0.18–0.71	0.44	0.19–2.2	0.78
Co	0.1–65	5.5	3–58	10	1–70	12	0.5–50	7.5	0.2–49	4.5
Cr	1.4–530	47	4–1100	51	5–500	83	11–195	77	1–100	12
Cu	1–70	13	4–100	23	6.8–70	23	6.5–140	24	1–113	16
F	<10–1100	130	<10–800	385	<10–840	360	10–1194	550	10–335	220
Hg	0.008–0.7	0.05	0.01–1.1	0.1	0.01–0.5	0.05	0.02–0.53	0.1	0.04–1.11	0.26
I	<0.1–10	2.3	0.3–8.3	1.7	0.3–9.5	3.4	0.3–10.8	2.4	1–10	4
Li	<5–72	22	1.4–130	46	6–105	56	9–175	53	0.01–3.2	1.3
Mn	7–2000	270	45–9200	525	50–7750	445	100–3907	480	7–2200	465
Mo	0.17–3.7	1.3	0.1–7.2	2.8	0.3–7.35	1.5	0.4–6.9	2	0.3–3.2	1.5
Ni	1–110	13	3–110	26	2–450	34	6–61	25	0.2–119	12
Pb	2.3–70	22	1.5–70	28	10–50	26	8–70	23	1.5–176	44
Sc	0.8–30	5	2.4–20	8	<5–15	8	<5–20	10	—	—
Se	0.005–1.32	0.25	0.02–1.9	0.34	0.1–1.4	0.38	0.1–1.2	0.33	0.1–1.5	0.37
Sr	5–1000	87	15–1000	210	15–1000	195	70–500	145	5–300	100
Ti	200–17,000	26,000	500–24,000	3300	400–10,000	4800	700–7000	3500	80–6700	2300
V	10–260	67	15–330	76	10–500	115	25–150	78	6.3–150	18
Zn	3.5–220	45	9–362	60	10–570	100	20–770	65	5–250	50

^a Ranges of common abundance in top soils and arithmetic means.

^b Soil units as given in [Table 3.1](#).

- Hydrolysis: reaction of minerals with water, producing new ions and/or insoluble components
- Oxidation: incorporation of the oxygen into the chemical components or increase of the element potential
- Reduction: reactions that are the reverse of oxidation
- Carbonatization: alteration of compounds into carbonates due to the incorporation of CO₂

All of these reactions are controlled by chemical equilibrium of the particular earth surface environment. The stability of such a system is often illustrated by Eh–pH diagrams for the given geochemical reaction.^{256,477} Despite the many questions raised and the difficulties in a practical evaluation of these diagrams, they clearly indicate that both factors—the redox system (Eh) and the buffer capacity (pH)—control physical and chemical properties of the soil. Theoretically, Eh and pH sums represent equilibrium constants, and they are estimated to range from 4 (for anaerobic soils) to 17 (for well-aerated soils).^{933,989} Redox condition of soils is expressed in mV units (Eh) as follows: (1) <300, anaerobic, (2) >330, partial oxidation, and (3) 750, full oxidation. Soils, however, are not at equilibrium. Especially soil-Eh is extremely variable. Measurements of soil-Eh and soil-pH may explain several thermodynamic processes that occur in the soil systems.^{933,1151}

The reactions of trace elements in a particular weathering environment are significantly different. Some generalizations of their properties as described by several authors are presented in Table 3.4. The mobility of these elements during weathering processes is determined first by the stability of the host minerals and second by the electrochemical properties of the elements. Fe, as the most common cation of variable oxidation stage in the weathering environments, is known to influence the behavior of the associated cations (Table 3.5).

The pattern of trace element distribution is usually a parameter that is very sensitive to changes of weathering environments. The so-called “chemical nature” of an element reflects mainly its electronegativity parameters and its ionic size. Selected elemental parameters of trace ions given in Table 3.6 may explain why individual trace elements reveal an affinity for association with major

TABLE 3.4
Behavior of Trace Elements in Various Weathering Environments

Degree of Mobility	Environmental Conditions	Trace Elements
High	Oxidizing and acid	B, Br, and I
	Neutral or alkaline	B, Br, F, I, Li, Mo, Re, Se, U, V, W, and Zn
	Reducing	B, Br, and I
Medium	Oxidizing and acid	Li, Cs, Mo, Ra, Rb, Se, Sr, F, Cd, Hg, Cu, Ag, and Zn
	Mainly acid	Ag, Au, Cd, Co, Cu, Hg, and Ni
	Reducing, with variable potential	As, Ba, Cd, Co, Cr, F, Fe, Ge, Li, Mn, Nb, Sb, Sn, Sr, Ti, U, and V
Low	Oxidizing and acid	Ba, Be, Bi, Cs, Fe, Ga, Ge, La, Li, Rb, Si, Th, Ti, and Y
	Neutral or alkaline	Ba, Be, Bi, Co, Cu, Ge, Hf, Mn, Ni, Pb, Si, Ta, Te, and Zr
Very low	Oxidizing and acid	Al, Au, Cr, Fe, Ga, Os, Pt, Rh, Ru, Sc, Sn, Ta, Te, Th, Ti, Y, and Zr
	Neutral or alkaline	Ag, Al, Au, Cu, Co, Fe, Ga, Ni, Th, Ti, Y, and Zr
	Reducing	Ag, As, Au, B, Ba, Be, Bi, Cd, Co, Cu, Cs, Ge, Hg, Li, Mo, Ni, Pb, Re, Se, Te, Th, Ti, U, V, Y, Zn, and Zr

Source: Data from Bieus, A. A., Grabovskaya, L. I., and Tikhonova, N. V., *Geochemistry of the Surrounding Environment*, Nedra, Moscow, 247, 1976 (Ru); Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 300, 1979 (Po); Panov, E. N., *Geokhimiya*, 10, 1568, 1980 (Ru); Rose, A. W., Hawkes, H. T., and Webb, J. S., *Geochemistry in Mineral Exploration*, Academic Press, London, 635, 1979.

TABLE 3.5**Association of Trace Cations with Iron Cations in Neutral or Slightly Acid Aqueous Phase**

Fe Oxidation Stage	Associated Cations
Fe ²⁺	Ti ³⁺ , Ti ⁴⁺ , V ³⁺ , V ⁴⁺ , Cr ³⁺ , Mn ²⁺ , Co ²⁺ , Pb ²⁺ , W ⁶⁺ , U ⁴⁺
Fe ³⁺	Ti ⁴⁺ , V ⁴⁺ , Cr ⁶⁺ , Mn ⁴⁺ , Co ³⁺ , Pb ⁴⁺ , W ⁶⁺ , U ⁶⁺

Source: Based on Polński, A., *Principles of Geochemistry*, Wyd. Geol., Warszawa, 634, 1988 (Po).

elements in various geochemical environments. The elements with an ionic potential below 3 predominate as free ions, while the elements with an ionic potential between 3 and 12 tend to form hydrolysates or complex ions. Easily mobile elements usually produce smaller hydrate ions in aqueous solutions than do more stable elements; also, the free energy (enthalpy) needed for the formation of their ions seems to be less than the energy required for ion formation of less mobile elements. Nieboer and Richardson¹⁰⁹⁹ proposed the classification of ions based on their coordination chemistry that describes the formation of ion/ligand complexes (Table 3.7). This classification gives general information on possible compounds that may be formed in specific environmental conditions. During weathering processes trace elements are released from primary minerals and fixed in/on secondary minerals (Kabata-Pendias,¹³⁵⁰ Soubrand-Colin et al., 2005). Geochemical properties of elements highly control their behavior during weathering and pedogenic processes (Table 3.8).

Trudgill¹¹⁶⁷ described that the amounts of cations solubilized by biological activity and by chelate action are usually much greater than those mobilized by the action of water and hydrolysis alone. The role of microorganisms (bacteria and fungi) and plants is of great importance in solubilizing minerals, and thus, in the input of chemical elements to the soil solution. These processes are known as biological weathering.

III PEDOGENIC PROCESSES

Pedogenic processes cannot be easily distinguished from weathering processes as they take place simultaneously and at the same sites. Most often they are closely interrelated. The main types of these processes include: (1) podzolization, (2) alkalization, (3) aluminization, (4) laterization, (5) sialization, (6) chelation, and (7) hydromorphic processes.

Several specific reactions, in addition to those involved in weathering, lead to the formation of a particular soil profile. Although there is a great diversity in pedogenic processes, they all include the following similar stages: (1) addition of organic and mineral materials to the soil, (2) losses of these materials from the soil, (3) translocation of these materials within the soil, both vertically and horizontally, and (4) transformation of organic and mineral matter in the soil.

These processes can be constructive or destructive in soil formation. Six factors that largely control the kind of soil that finally develops are: (1) climate (temperature, rainfall), (2) vegetation and other soil biota, (3) parent material (kind of minerals), (4) topography (open or closed systems), (5) time, and (6) anthropogenic activity (degradation, contamination, and remediation).

Soil parameters depend on several processes, of which the most important are: (1) pH and Eh values, (2) amount and mineral composition of fine granulometric fraction, (3) amount and kind of organic matter, (4) oxides and hydroxides of Fe, Mn, and Al, and (5) microorganisms.

The classification of soil units very commonly is based on the factors predominating soil-forming processes (Table 3.1). Pedogenic processes stimulated mainly by climate predominate, but soils influenced most strongly by parent material or vegetation are quite frequent. Recently anthrosols/anthroposols formed under a predomination of man's activity became relatively common.

TABLE 3.6
Geochemical Associations and Some Properties of Trace and Major Elements

Major Elements (boldface) and Associated Trace Element	pH of Hydrous Oxide Precipitation	Ionic Radii (Å)	Electronegativity (kcal/g atom)	Ionic Potential (charge/radius)	Diameter of Hydrated Ion in Aqueous Solution (Å)
K ⁺	—	1.7–1.6	0.8	0.6	3.0
Na ⁺	—	1.2–1.1	0.9	0.9	4.5
Cs ⁺	—	2.0–1.9	0.7	0.5	2.5
Rb ⁺	—	1.8–1.7	0.8	0.6	2.5
Ca ²⁺	—	1.2–1.1	1.0	1.8	6.0
Mg ²⁺	10.5	0.8	1.2	2.5	8.0
Sr ²⁺	—	1.4–1.3	1.0	1.5	5.0
Ba ²⁺	—	1.7–1.5	0.9	1.3	5.0
Pb ²⁺	7.2–8.7	1.6–1.4	1.8	1.9	4.5
Se ³⁺	—	0.8	1.3	3.7	9.0
Fe ²⁺	5.1–5.5	0.9–0.7 ^a	1.8	2.6	6.0
Cu ²⁺	5.4–6.9	0.8	2	2.5	6.0
Ge ⁴⁺	—	0.5	1.8	8.3	—
Mo ⁴⁺	—	0.7	—	5.5	—
Mn ²⁺	7.9–9.4	1–0.8	1.5	2.0	6.0
Zn ²⁺	5.2–8.3	0.9–0.7	1.8	2.6	6.0
Fe ³⁺	2.2–3.2	0.7–0.6 ^a	1.9	4.4	9.0
Co ²⁺	7.2–8.7	0.8–0.7	1.7	2.6	6.0
Cd ²⁺	8.0–9.5	1.03	—	—	—
Ni ²⁺	6.7–8.2	0.8	1.7	2.6	6.0
Cr ³⁺	4.6–5.6	0.7	1.6	4.3	9.0
Mn ⁴⁺	—	0.6	—	6.5	—
Li ⁺	—	0.8	1.0	1.2	6.0
Mo ⁶⁺	—	0.5	1.8	12.0	—
V ⁵⁺	—	0.5	—	11.0	—
Al ³⁺	3.8–4.8	0.6–0.5 ^a	1.5	5.6	9.0
Be ²⁺	—	0.3	1.5	5.7	8.0
Cr ⁶⁺	—	0.4	—	16.0	—
Ga ³⁺	3.5	0.7–0.6	1.6	4.9	—
La ³⁺	—	1.4–1.3	1.1	2.3	9.0
Sn ²⁺	2.3–3.2	1.3	1.8	1.5	—
Y ³⁺	—	0.9	1.2	3.1	—
Si ⁴⁺	—	0.4	1.8	12.0	—
Ti ⁴⁺	1.4–1.6	0.7	1.5	5.8	—
Zr ⁴⁺	2.0	—	1.4	4.3	11.0

^a Values given for high and low spin, respectively.

Initially, at early stages of weathering and pedogenic processes, the trace element composition of the soil is inherited from the parent material. With time, however, the trace element status of soil will become different due to the influence of predominating pedogenic and anthropogenic processes (Table 3.9). The comparison of trace element concentrations in soils with their concentrations in parent material is often used as a factor of their mobility during pedogenic processes. However,

TABLE 3.7
Classification of Ions Based on the Formation of Complexes

Class	Ions
Oxygen seeking	Cs ⁺ , Li ⁺ , Ba ²⁺ , Sr ²⁺ , La ³⁺ , Gd ³⁺ , Lu ³⁺ , Y ³⁺ , Be ²⁺ , Sc ³⁺
Borderline	Cd ²⁺ , Sn ²⁺ , Pb ²⁺ , Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Cr ²⁺ , V ²⁺ , Zn ²⁺ , Mn ²⁺ , Ti ²⁺ , In ³⁺ , Ga ⁺ , Sb ³⁺⁻ , As ³⁺⁻ , Sn ⁴⁺⁻
Nitrogen/sulfur seeking	Au ⁺ , Ag ⁺ , Cu ⁺ , Tl ⁺ , Hg ²⁺ , Pd ²⁺ , Pt ²⁺ , Bi ³⁺ , Ti ³⁺ , Pb ⁴⁺⁻

Source: From Nieboer, E. and Richardson, H. S., *Environ. Pollut., Ser. B.*, 3, 1980. With permission.

the dilution by organic matter should be considered when making meaningful judgments on the accumulation or migration of these elements during weathering and soil formation. The fate of trace elements mobilized by dissolution of the host minerals or compounds depends on the properties of their ionic species formed in the soil solution (Tables 3.10) and is governed by the variable chemical system of a soil that can be characterized as follows:

- Heterogeneous distribution of compounds
- Seasonal and spatial alterations in major master variables, as pH, Eh
- Transformation of species: (1) electron transfer reactions, (2) ligand exchange reactions, (3) organometallic reactions, (4) biotransformations
- Transfer between phases: (1) adsorption reactions, (2) diffusion–absorptions into solids, (3) diffusion to solution phase, (4) formation of solid phase, (5) coprecipitation, (6) coagulation
- Biouptake and bioaccumulation

TABLE 3.8
Geochemical Classification of Trace Elements^a

Siderophile	Chalcophile	Lithophile
6: Mo	5: (Ta)	1: Li, Rb, Cs
7: Re	6: (Mo)	2: Be, Sr, Ba, Ra
8: Fe, Ru, Os	8: Fe, Ru	3: Sc, Y, Lanthanides, Actinides
9: Co, R, Ir	9: (Co),	4: Ti, Zr, Hf
10: Ni, Pd, Pt	10: (Ni), (Pd), (Pt)	5: V, Nb, Ta
11: Au	11: Cu, Ag	6: Cr, Mo, W
14: Ge, Sn, (Pb)	12: Zn, Cd, Hg	7: Mn,
15: As	13: Ga, In, Tl	8: (Fe)
	14: (Ge), (Sn), Pb	9: (Co)
	15: As, Sb, Bi	10: (Ni)
	16: Se, Te	12: (Zn), (Cd)
		13: B
		14: (Ge), (Sn), (Pb)
		15: (As)
		17: F, Cl, Br, I

Bold numbers are groups in the Periodic Table.

Symbols within parentheses are given not for main geochemical tendencies of an element.

^a Based on data after Rankama and Sahama (*vide* Fairbridge, 1972).

TABLE 3.9
Principal Types of Soil-Forming Processes and Trends in the Behavior of Trace Elements

Process	Most Favorable Climatic Zone	RSG Code ^a	Behavior of Trace Elements in Surface Soil	
			Accumulation	Migration
Podzolization	Cold northern	AB, AC, PZ, LV	Co, Cu, Mn, Ni, Ti, V, Zn (in illuvial horizon)	B, Ba, Br, Cd, Cr, I, Li, Mn, Rb, Se, Sr, V, Zn
Aluminization	Cool and humid temperate	CM, LV, PL, PZ	Co, Mn, Mo, V (in gleyed horizon)	B, Ba, Br, Cu, I, Se, Sr
Siallization	Warm temperate and dry tropical	KS	B, Ba, Cu, Mn, Se, Sr	—
Lateritization	Humid tropical	FR, PT	B, Ba, Cu, Co, Cr, Ni, Sr, Ti, V	—
Alkalinization	Warm with dry sea-seasons	LP, PL	B, Co, Cr, Cu, Mo, Ni, Se, Zn, V	—
Hydromorphic formation	Intrazonal soils	—	B, Ba, Co, Cu, I, Mn, Mo, Se, Sr, U (in organic horizon)	B, Br, Co, Cu, Mn, Ni, U, V

^a Code for the Reference Soil Group as given in Table 3.1.

Concentrations of trace elements in soil solution are closely correlated with their mobility and availability. However, the soil solution is constantly changing in chemical composition. In the solution of some soils, Cd, Cu, and Zn are likely to predominate in forms of free ions, up to over 90% of their total concentrations (Silveira et al., 2007). There is observed a strong correlation

TABLE 3.10
Some Inorganic Ionic Species^a of Trace Elements and Iron Occurring in Soil Solution^b

Element	Cations	Anions
Ag	Ag ⁺	AgCl ₂ ⁻ , AgCl ₃ ²⁻ , Ag(SO ₄) ₂ ²⁻
As	As ³⁺	AsO ₅ ⁻ , HAsO ₄ ²⁻ , H ₂ AsO ₃ ⁻
B		BO₃³⁻ , H ₂ BO ₃ ⁻ , HBO ₃ ²⁻
Be	Be ²⁺ , BeOH ⁺	BeO ₃ ²⁻ , Be(OH) ₃ ⁻ , Be(CO ₃) ₂ ²⁻
Cd	CdCl ⁺ , CdOH ⁺ , CdHCO ₃ ⁺ , CdHS⁺	CdCl ₃ ⁻ , Cd(OH) ₃ ⁻ , Cd(OH)₄²⁻ , Cd(HS)₄²⁻
Co	Co ²⁺ , Co ³⁺ , CoOH ⁺	Co(OH) ₃ ⁻
Cr	Cr ³⁺ , CrOH ²⁺	HCrO ₃ ²⁻ , CrO ₄ ²⁻ , Cr(OH) ₄ ⁻ , Cr(CO ₃) ₃ ³⁻
Cu	Cu ²⁺ , CuOH ⁺ , Cu ₂ (OH) ₂ ²⁺	Cu(OH) ₃ ⁻ , Cu(OH)₄²⁻ , Cu(CO ₃) ₂ ²⁻
F	AlF ²⁺ , AlF ₂ ⁺	F ⁻ , AlF ₄ ⁻
Fe	Fe ²⁺ , FeCl ⁺ , Fe(OH) ₂ ⁺ , FeH ₂ PO ₄ ⁺	Fe(OH) ₃ ⁻ , Fe(OH)₄²⁻ , Fe(SO ₄) ₂ ⁻
Hg	Hg ₂ ²⁺ , HgCl ⁺ , HgCH ₃ ⁺	HgCl ₃ ⁻ , HgS₂²⁻
I		I ⁻ , I ₃ ⁻ , IO ₃ ⁻ , H₄IO₆⁻
Mn	Mn ²⁺ , MnOH ⁺ , MnCl ⁺ , MnHCO ₃ ⁺	MnO ₂ ⁻ , HMnO ₂ ⁻ , Mn(OH) ₃ ⁻ , Mn(OH)₄²⁻
Mo		MoO ₄ ²⁻ , HMoO ₄ ⁻
Ni	Ni ²⁺ , NiOH ⁺ , NiHCO ₃ ⁺	HNiO ₂ ⁻ , Ni(OH) ₃ ⁻
Pb	Pb ²⁺ , PbCl ⁺ , PbOH ⁺	PbCl ₃ ⁻ , Pb(CO ₃) ₂ ²⁻
Se		SeO₃²⁻ , SeO ₄ ²⁻ , HSe⁻ , HSeO ₃ ⁻
V	VO ²⁺	H ₂ VO ₄ ⁻ , HVO ₄ ²⁻ , VO ₃ ⁻
Zn	Zn ²⁺ , ZnCl ⁺ , ZnOH ⁺ , ZnHCO ₃ ⁺	ZnO ₂ ²⁻ , Zn(OH) ₃ ⁻ , ZnCl ₃ ⁻

^a The symbols given in bold letters indicate the ions occurring only in extreme pH and Eh regimes.

^b After Kabata-Pendias and Sadurski (2004).

between soil pH and free ion species, whereas the presence of SO_4^{2-} highly decreases the activity of metal species. Mineral particles of biological composition (prosits) and some organic compounds (proteins) may also occur in soil solution and decreases amounts of free ion species (Keller, 1997; Rigou et al., 2006). Sauvé et al.¹⁴⁷⁸ calculated free metal activity (pCu^{21} and pPb^{21}) in the soil solution based on the total Cu, pH, and soil organic matter. They concluded that these values help in a prediction of toxic effects on crops and biological activity of soils and are also appropriate for other metals.

Biological, chemical, and physical characteristics of such natural systems as soils have chemical gradients with depth and also have significant seasonal alterations of some major master variables. The lack of accurate *in situ* measurements of these critical chemical parameters and the lack of determinations of their distribution and variability at the level of individual soil pores and particles is an important limitation in our understanding of the chemical context of the soil system.

Dynamic equilibrium between soil components is governed by various interactions between the solid and gaseous phases of soil, the biota, and the soil solutions, as is illustrated by Figure 3.3. The electrochemical properties of elements and the stability of host minerals control the mobility of trace elements. In an arid environment, physical weathering generally occurs, chemical transformation being rather poor due to the lack of water. In a tropical climate with high temperature and humidity, chemical weathering is favored, resulting in the formation of more clay minerals. Several studies of kinetics of reactions in the soil system were conducted recently, and some principles, mechanisms, and models were described and proposed.^{1151,1154} The chemical forms governing the mobility and phytoavailability of trace metals and residence times of trace pollutants in the soil layers have been the main subjects of mechanistic modeling and calculations. Sparks¹¹⁵¹ stated that thermodynamic data can predict only the final state of a system from an initial nonequilibrium mode. However, kinetic data provide valuable insights into the reaction pathways and into the mechanisms of chemical reactions in the complex multiphase soil system. This author (Sparks,

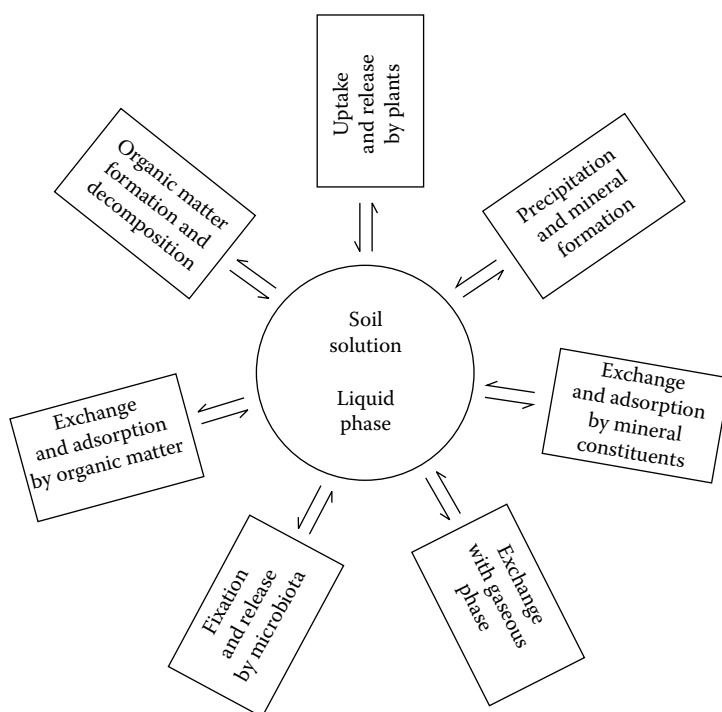


FIGURE 3.3 Schematic interactions between soil components and compartments.

TABLE 3.11
Surface Area and Sorption Capacity (CEC) of Some Soil Minerals^a

Mineral	Total or Specific Surface (m ² /g)	CEC ^b (cmol(+)/kg)
Allophanes	100–880	5–350
Kaolinite	7–30	3–22
Halloysite	10–45	3–57
Montmorillonite	280–800	80–150
Illite	65–100	20–50
Chlorite	25–150	10–40
Vermiculites ^c	50–800	10–200
Gibbsite	25–58	50 ^d
Goethite	41–81 (305–412) ^e	160
Mn-oxides	32–300	150–230
Imogolite	900–1500	30–135
Zeolite	720	350–615
Palygorskite	5–30	—
Sepiolite	20–45	21–24
Muscovite	60–100	10–40
Biotite	40–100	10–40
Quartz	2–3	7

^a Data sources: Baldock and Nelson, 2000; Bolt, 1979; Brümmer⁹⁵⁴; Tan, 1998; Sparks 1995.

^b CEC, cation exchange capacity.

^c Dioctahedral and trioctahedral vermiculites.

^d Amorphous Al-oxides.

^e Amorphous Fe-oxides (in parentheses).

2000) emphasized that more studies on Mn and other hydroxides are needed for understanding and assessment of redox processes in soils.

The affinity of trace elements for soil constituents is strongly influenced by their electrochemical properties and is closely related to the specific surface area and cation exchange capacity (CEC) of minerals. Some clay minerals, such as montmorillonite, imogolite, vermiculite, and amorphous allophanes reveal the highest sorption capacity (Table 3.11).

Due to the variable charge of both clays and organic particles, different organo-mineral complexes are formed that may greatly influence element mobility in soils (Tan, 1998). This author has emphasized that various bindings between microorganisms, like bacteria and fungi, and soil clays and organic matter, may also occur and may have serious environmental importance. It is evident that Fe/Mn-rich particulates and hydrogen sulfide are most significant among the abiotic factors in controlling trace metal behavior in the terrestrial environment (Sparks, 1995; Bartlett¹²¹⁹). The relationship between Fe contents and some trace metals indicates an impact of soil Fe on the distribution of some trace metals.

A DISSOLUTION AND MOBILIZATION

Chemical reactions leading to the mobilization of each species of ions can be characterized by thermodynamic equations. At each equilibrium state the reaction rates of both directions compensate and keep the composition of the soil phases (solid, liquid, and gaseous) constant.

Chemical equilibria of various soils have been studied and comprehensive mathematical models for the particular soil conditions are presented by Bolt and Bruggenwert. The diversity of ionic species of trace elements and their various affinities to complexes with inorganic and organic ligands

make possible the dissolution of each element over a relatively wide range of pH and Eh. Each element can also be quite readily precipitated and/or adsorbed, even under a small change of the equilibrated conditions. In soils, solubility equilibria may change significantly within a few centimeters (even millimeters) at both horizontal and vertical soil gradients. Thus, these equilibria are local and may often be quite different in various sites of the soil. Since the dynamic nature of soil components causes dissolution and precipitation, many of the minerals and amorphous solids may not be in equilibrium under soil conditions.

Mechanisms of trace element mobility have been broadly investigated recently. Several models and equations are proposed to simulate and predict trace elements behavior in terrestrial environments. Soil processes and parameters that control trace element status in soils are presented by Carrillo-Ganzález et al. (2006). Navas et al. (2005) used the natural gamma-emitting radionuclides to study the behavior of major and trace elements in soils. The authors concluded that soil properties such as pH, carbonates, and Fe and Mn oxides greatly influence the behavior of chemical elements. Impellitteri et al. (2001), on the other hand, reported that soil pH and OM are the most important parameters determining trace metal partitioning and aqueous speciation in soils.

Many textbooks present stability diagrams for ionic species of trace elements as functions of pH and Eh.^{166,256,477} Selim and Amacher (2001) presented an overview of several models to describe retention and release of trace metals Table 3.6 in soils. In natural soil conditions, pH ranges most often between 5 and 7, and Eh ranges between 400 and 2200 mV, except where there are high reduction states in waterlogged soils. The properties of ionic species of each element vary, and the pH range for precipitation of their hydrous oxides is flexible. One can, however, conclude that usually the most mobile fractions of ions occur at a lower range of pH and at a lower redox potential, which is illustrated in Figure 3.4.

It can be anticipated that with increasing pH of the soil substrate, the solubility of most trace cations will decrease. Indeed, the concentration of trace elements is lower in soil solutions of alkaline and neutral soils than in those of light acid soils (Table 3.12). Spósito¹¹⁵³ investigated the chemical thermodynamics and its applicability to the soil solution and described possible systems of trace cation exchange.

Determination of various species (operational groups) of trace elements is broadly used, especially for two purposes: to link with the potential bioavailability, and to predict the mobility affecting their

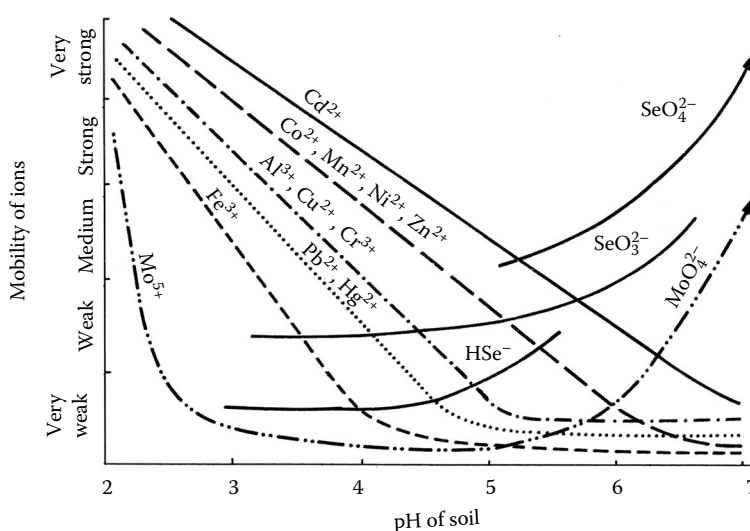


FIGURE 3.4 Schematic trends in the mobility of metals as influenced by soil pH. (Data for light mineral soil.)

TABLE 3.12**Trace Elements ($\mu\text{g/L}$) in Soil Solutions Obtained by Centrifugation from Soils of Various pH Values^a**

Element	Soil Type and Range of pH Values				
	Acid Sandy (2.5–4)	Sandy (4–4.5)	Silty (5.5–6.5)	Loamy (7–7.5)	Calcareous (7.5–7.8)
B	nd	nd	nd	200	800
Cd	107	nd	nd	nd	nd
Co	nd	nd	nd	0.5	5
Cu	783	76	20	50	50
Fe	2223	1000	500	200	100
Mn	5965	8000	5000	100	700
Mo	nd	nd	nd	5	3
Pb	5999	nd	nd	nd	nd
Zn	7137	1000	5000	100	300

Note: Values are arithmetic means of five samples. “nd”—not determined.

^a After Kabata-Pendias, A. and Wiecek, K., *Soil Sci. Ann.*, 36/4, 33, 1985.

transport within the soil profile and to ground waters. Various concentrations of different reagents and variable soil/solution ratios over broad pH ranges are used for the selective extraction procedures (Kabata-Pendias and Sadurski, 2004). In consequence, each method gives operational groups of metals that are not comparable. However, they give an approximate fractionation of metals occurring in soils which are, in general: (1) easily exchangeable or water soluble, (2) specifically sorbed, for example, by carbonates, or phosphates, (3) organically bound, (4) occluded by Fe/Mn oxides and hydroxides, and (5) structurally bound in minerals (residual). Gupta and Gupta (2005) emphasized that in spite of achievements in elaboration of several extraction methods, there is a need to develop methods for anion (especially Mo and Se) testing.

Recently a number of papers have been published on the widely applied BCR three-step sequential extraction for the determination of the operationally defined speciation or fractionation of trace metals in soil and sediment samples (Giacomelli et al., 2002; Tokalio Glu et al., 2003; Shober et al., 2007; Medved et al., 2008). This procedure has been proposed to harmonize the methodology throughout the European Union and to improve comparability between results of Measurements and Testing Program of the European Union (SM&T—formerly BCR—the Community Bureau of Reference). Mosson and Davidson (2003) concluded that there is no clear improvement in precision obtained with use of this method, original or modified. However, it is possible that this would be more evident in interlaboratory trials.

The speciation of trace metals in soils is not stable and relatively easy transformation of their forms in soils is observed. Mäkelä-Kurtto (2000) investigated the impact of land use on the speciation of trace metals (Cd, Cu, Pb, Zn) and reported a significant variation between land-use types, in addition to parent material and soil horizons. A very comprehensive review of the application of single and sequential extraction procedures to soil is presented by Rao et al. (2008). The authors concluded that there is an urgent need for faster and more reliable methods for the soil pollution assessment.

Most often, the mobility of trace metals, especially of Cd, Cu, Cr, and Zn, increases in poorly aerated (low oxidation stage, $E_h < 100$ mV) soils. However, increasing Cd solubility with increasing E_h up to >200 mV was also observed.¹⁴²⁵ The effect of redox potential on availability of Cd, Cu, and to a smaller degree Zn, was reported by Gambrell and Patrick.¹³⁰⁴ Chuan et al.¹²⁵⁸ described that acidic and reducing soil conditions are more favorable for trace metal solubilization, and the effect

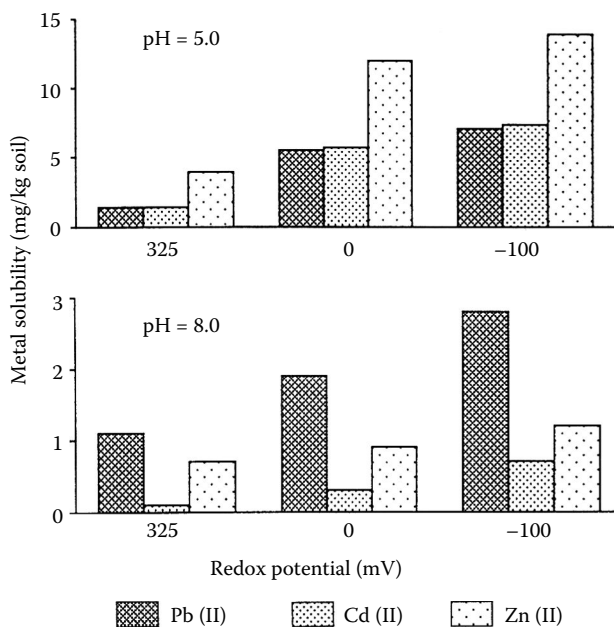


FIGURE 3.5 Impact of redox potentials on the solubility of soil trace metals in water at pH 8.0 and 5.0. (From Chuang, M. C., Shu, G. Y., and Liu, J. C., *Water Air Soil Pollut.*, 90, 543, 1996. With permission.)

of pH is more significant than that of redox potential (Figure 3.5). Fontes and Alleoni (2006) highlighted the impact of electrochemical soil properties on behavior of trace elements.

Karczewska and Milko (in press) studied solubility of Cu, Pb, and Zn under extraction by different chelating agents. The highest mobility, by all agents, was for Cu and the lowest for Zn. The EDTA chelating agent was the most effective for all metals. The extraction with Mehlich-3 solution has been reported as very effective for the determination of phytoavailable Cd, Cu, Ni, Pb, and Zn (Fontes et al., 2008). Fontes and Alleoni (2006) emphasized that trace element speciation and adsorption models for highly weathered soils from the humid tropics need better understanding. Takeda et al. (2006) investigated several commonly applied extraction methods for the phytoavailability assessments of 28 elements and concluded that the extracted fractions of elements using these solutions did not correlate with the concentration in plant samples for most elements. There were, however, some relationships but for a given extraction and a given element. Evangelou et al. (2007) studied effects of different chelating agents on metals and summarized that the research on phytoextraction should be continued, enabling the discovery of new mobilizing agents, but there is a question whether more studies will lead to progress in this field. The key concepts on metal bioavailability are presented by Basta et al. (2005). The authors suggested that research is needed to determine the effect of residuals on trace element behavior in soil, especially in the long-term period. They also suggested variability in the trace cation sorption by SOM and NOM. Bini and Gaballo (2006) emphasized that in Anthrosols behavior of some trace metals may significantly differ from that in “normal” soils. Depending on the variability in physico-chemical characteristics of trace metals (TMs), their affinities to soil components govern their fractionation (Figure 3.6).

Smith and Huyck¹⁵⁰¹ studied metal mobility under different environmental conditions. Although it is difficult to predict the element mobility in various environmental compartments, the authors referred to the capacity of an element to move within fluids after dissolution. The following conditions and behaviors of trace metals are distinguished:

- Oxidizing and acid, pH 3: (i) very mobile—Cd, Co, Cu, Ni, and Zn; (ii) mobile—Hg, Mn, Re, and V; and (iii) somewhat mobile and scarcely mobile—all other metals.

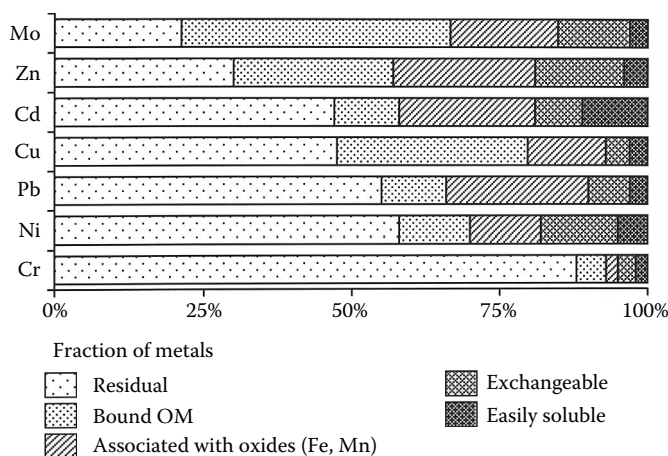


FIGURE 3.6 Fractionation of trace metals in soils (in percent of total content). Data for Mo are for the chernozem, and all other metals for the podzolic loamy sand. (Based on data from Čumakov and Neuberg¹⁵⁴, *Bilanz in der Spurenelemente in der Pflanzenproduktion der Tschechoslovakei, Phosphorsaure*, 1970) and Kabata-Pendias and Piotrowska³⁸², *Total Contents of Trace Elements in Soils of Poland, Mat. IUNG*, 1971.)

- Oxidizing in the absence of abundant Fe-rich particulates, pH 5: (i) very mobile—Cd and Zn; (ii) mobile—Mo, Re, Se, Sr, Te, and V; and (iii) somewhat mobile and scarcely mobile—all other metals.
- Oxidizing with abundant Fe-rich particulates, pH 5: (i) very mobile—none; (ii) mobile—Cd and Zn; and (iii) somewhat mobile and scarcely mobile—all other metals.
- Reducing in the absence of hydrogen sulfide, pH 5: (i) very mobile—none; (ii) mobile—Cd, Cu, Fe, Mn, Pb, Sr, and Zn; (iii) somewhat mobile and scarcely mobile—all other metals.
- Reducing with hydrogen sulfide, pH 5: (i) very mobile—none; (ii) mobile—Mn and Sr; and (iii) scarcely mobile to immobile—all other metals.

It is evident that Fe-rich particulates and hydrogen sulfide are among the abiotic factors most significant in controlling trace metal behavior in the terrestrial environment. Ankley et al.¹²⁰² included the acid-volatile sulfide system in developing the sediment quality criteria (SQC), which clearly refers to a crucial impact of sulfides on the behavior of metals in sediments.

The solubility of trace elements in soil has great significance in their bioavailability and their migration. “Heavy” soils (rich in clay fractions), both neutral and alkaline, provide good storage for trace elements and will supply them to plants at a slow rate. This slow release may, however, cause deficiency effects of certain micronutrients to develop in plants. “Light” soils (rich in sandy fraction), on the other hand, can be a source of easily available trace elements during a relatively short period of time. These soils can also lose their pool of available micronutrients at quite a high rate.

The aqueous phase of soil, soil solution, is composed of water with colloidal suspension and dissolved substances, which can be free salts and ions of various elements, organic and mineral-organic compounds. In addition to simple ionic species (Table 3.10), various complex compounds, including bio-inorganic complexes occur. Various ion pairs, of specific forms of oppositely charged ions that are thermodynamically stable, can also occur in solutions as manifold and of variable compositions. Common ion pairs, mainly hydroxides, in soil solution are, for example: CdOH^+ , CuOH^+ , FeCl^+ , ZnHCO_3^+ , PbSO_4^0 . Complex compounds of a relatively high stability constant occurring in soils solution are: CdCl_2^0 , Cd(OH)_2^0 , CdSO_4^0 , Co(OH)_2^0 , Cr(OH)_3^0 , Cu(OH)_2^0 , FeCl_2^0 , FeCl_3^0 , Hg(OH)_2^0 , MnSO_4^0 , Ni(OH)_2^0 , PbSO_4^0 , Pb(OH)_2^0 , VO(OH)_3^0 , Zn(OH)_2^0 (Kabata-Pendias and Sadurski, 2004).

Some of the first studies of soil solutions conducted by Hodgson et al.³²⁰ indicated that appreciable quantities of trace elements are present as complexes, mainly with organic ligands. Inorganic

complexes may, however, also be of importance for the particular element and condition. The concentrations of trace elements in soil solutions vary considerably among soils and with time. Great fluctuations have been observed under the influence of the following factors: (1) time, (2) vegetation, (3) microbial activity, (4) waterlogged state, and (5) heterogeneity of the solid soil phase.

Knowledge of the total composition of the soil solution or any nutrient solution is essential for predicting plant uptake of nutrients or plant growth. The partitioning of trace elements between the soil and soil solution determines their mobility and bioavailability. However, predicting the properties of soil solution is difficult, and sophisticated techniques must be adopted for obtaining the undiluted soil solution. Moreover, methods used for obtaining solutions from soils differ widely; therefore, it is difficult to adequately determine mean concentrations of trace elements. The range of trace element concentrations, as measured in various soil solutions (obtained by different techniques), vary widely ($\mu\text{g/L}$): Cd, 0.2–300; Co, 0.3–87; Cu, 1–135; Mn, 25–8000; Ni, 3–150; Pb, 0.6–65; Zn, 1–17,000.

Vaselli et al.¹⁵³¹ measured trace metal concentrations in soil solution by means of zero-tension microlysimeters from two pedological horizons of the Xerochrept forest soil in Tuscany (Italy). Concentrations of these metals varied significantly with time of collection, especially in the solution obtained from the A horizon; for example, range (in $\mu\text{g/L}$) for Zn was 35–1586, Cu 9–131, Mn 5–200, Ni 1–50, Cr 2–44, Pb 1–17, and Cd 0.1–0.9. Metal contents in solution from the B horizon were most stable and indicated significantly higher amounts of Ni (range 31–92 in $\mu\text{g/L}$) and Cr (range 3–154 $\mu\text{g/L}$). The authors explained this phenomenon as an effect of weathering of parent material enriched in these metals.

Rainfall, evaporation, and plant transpiration can change trace element concentrations in soil solutions more than tenfold, whereas the observed variations for major ions (Ca, Mg, K, Na, NO_3 , and PO_4) are much less. Acidification increases the intensity by which trace metals are mobilized in soils. The concentration of metals in the solution of the very acid soil was 9080 $\mu\text{g/L}$ (the sum of Fe, Mn, Zn, Pb, Cu, and Cd), whereas the solution of the same kind of soil, but with neutral range of pH, contained 17 $\mu\text{g/L}$ of these cations.¹⁰⁴⁸

The uptake of a given ion depends not only on its activity in the solution but also on the activities of other ions and the relation that exists between solution ions and exchangeable or solid-phase ions. However, the transfer of chemical elements between soil compartments and plants do not necessarily go through the liquid phase. Several direct exchanges at the surface of phases and compartments are possible. Free metal ion activity (FMI) in the soil solution controls cationic availability and toxicity. Procedures for the determination of FMI are discussed by Pampura et al. (2007).

Soluble major ions greatly influence the quantities of soluble trace elements. Solutions of most soils contain an excess of Ca, which in many soils constitutes more than 90% of the total cation concentration. Ca is, therefore, the most important cation in governing the soluble stage of trace elements in soils. There are examples, however, of soils in which complexing trace cations prevent precipitation in the presence of Ca^{2+} and in soil solutions having a relatively high pH level. Thus, more than normal concentrations of dissolved metal ions in solutions and the ready uptake of trace elements by plants usually are related to the formation of complexes. This possibility is also suggested by the observation that half of the calcium in soil solutions is usually present as an organic complex.³⁵⁶ The anionic composition of soil solutions is also of importance in controlling the trace element status. Little is known, however, about the relation of trace elements to anionic species in soil solutions.

Different complexing tendencies of cations to interact with ligands can be explained by the rules of coordination chemistry. It is possible, therefore, to predict that certain cations more readily complex a particular ligand. Thus, some metallic ions such as Be^{2+} , Cr^{3+} , and Co^{3+} will react readily with PO_4^{3-} , CO_3^{2-} , NO_3^- , and organic amines and so on; the group including Ni^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , and Sn^{2+} may more easily complex Cl, Br, NO_2 , and NH_3 , while cations of the chemical nature of Hg^{2+} , Ag^+ , and Tl^+ are likely to link with complexes of I, CN, CO, S, P, and As.

In a soil solution, organic compounds and water are the most abundant ligands; therefore, hydrolysis and organic complexing are the most common reactions. These reactions are pH sensitive and can be correlated with the size and charge of the cations. Higher ionic potentials usually indicate a

higher degree of hydration in the solution, thus an easier precipitation. The range in pH for the precipitation of hydrous oxides of some cations (Table 3.6) illustrates that the order of cation mobility in an aqueous phase under an oxidation regime of soil may decrease as follows: $\text{Mg}^{2+} = \text{Ca}^{2+} > \text{Ag}^+ > \text{Hg}^{2+} > \text{Mn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} = \text{Co}^{2+} = \text{Pb}^{2+} > \text{Be}^{2+} > \text{Zn}^{2+} = \text{Cu}^{2+} > \text{Cr}^{3+} > \text{Bi}^{3+} > \text{Sn}^{4+} > \text{Fe}^{3+} > \text{Zr}^{4+} > \text{Sb}^{3+}$. However, the application of data on heavy metal activity in pure systems to soils can only be informative because of various effects of complex ion formation, solid solution, and coating. Rose et al.¹¹³¹ discussed general rules governing the mobility and transport of chemical elements in aqueous solutions of the surficial environment and emphasized that the transition elements with incomplete inner electron shells (e.g., most of trace metals) are slightly soluble and strongly adsorbed by media.

The mobility of trace elements in soils evidently depends on complex formation. However, most of the species of trace elements, especially cations, are slightly soluble, and only small proportions occur in the aqueous phase. The total content of trace cations generally ranges from 10 to 100 $\mu\text{g/L}$ in a solution of normal soils, while in contaminated soils these values can be much higher (Kabata-Pendias³⁷⁵). When soluble compounds of trace metals are added to soils, their concentrations increase in equilibrated solutions with increasing doses of added metals. In an experiment conducted by Cottenie et al.,¹⁴⁸ the relative solubility of the added metals at the highest dose rate in light sandy soil was as follows: 39% of 1000 mg Zn/kg, 50% of 5000 mg Cu/kg, 30% of 5120 mg Cd/kg, and 26% of 2695 mg Pb/kg.

Bujtas et al.¹²⁴⁶ studied the solubility rate of metals added with sewage sludge enriched in metals (Cd, Cr, Ni, Pb, and Zn) to soils. The transfer factor, calculated as a ratio of metals in a solution of highly contaminated soil to their contents in a solution of control soils, decreases in the following order: Cd 1804 > Ni 604 > Zn 563 > Pb 156 > Cr 4. These results clearly indicate extremely easy solubility of Cd under soil conditions of brown forest soil at pH (KCl) about 5.0. For sandy acid soils, values of the transfer factor were even higher. On the other hand, Csillag et al.¹²⁶⁵ concluded that the transfer of these metals applied to soil in forms of sludges was rather negligible when amounts of added metals corresponded to the official limits. Shober et al. (2007) reported that biosolids applications increased trace metal contents in all soil fractions, especially Cu and Zn in mobile fractions. However, loadings of these metals were much smaller than cumulative loadings permitted under USEPA.

B VOLATILIZATION

Volatilization of certain trace elements from surface soil is a relatively common process and is considered to be associated mainly with As, Hg, I, and Se cycling. However, these processes are also observed in the case of Bi, Cd, Pb, and possible other metals and metalloids. Volatilization due to the microbial transformation of elements into forms of volatile organic compounds, mainly methylated forms, is relatively common mechanism. Methylation of elements by living cells, mainly prokaryotic microorganisms, is a relatively well-known mechanism. Formation of bonds between methyl groups and elements alters various physical properties such as solubility or volatility. This alteration enhances the mobility of the trace metals and can play a major role in the environmental cycles for these elements. However, despite the relevance of these processes, their mechanisms are not yet well understood.

The methylation reactions proceed through the formation of a methylated element in surface soil and are followed by the movement of an element out of the solid lattice into the surrounding air or solution. Impact of various soil parameters on Hg methylation is discussed by Grigal (2002).

C SORPTION AND ADSORPTION

Soils are considered as sinks for trace elements; therefore, they play an important role in environmental cycling of these elements. They have a great ability to fix many species of trace ions. The

term “sorption” used in this chapter refers to all phenomena at the solid-solution boundary, including the following intermolecular interactions:

- Van der Waals’ forces
- Ion-dipole forces
- Hydrophobic and hydrogen bondings
- Charge transfer
- Ion and ligand exchanges
- Chemisorption
- Magnetic bonding

Adsorption/desorption reactions occurring all the time in soil control basic soil properties. Sparks (1999) presented several models for adsorption and cation exchange. The main process in the sorption is cation exchange between soil solution and soil components (both inorganic and organic). Every soil component is active and affects soil solution ion concentration either by precipitation-dissolution reactions or by ionic interactions with phase surfaces. Soil components involved in the sorption of trace elements are: (1) oxides (hydrous, amorphous), mainly of Fe and Mn and, to a much lesser extent, Al and Si, (2) clay minerals, (3) organic matter and biota, and (4) carbonates, phosphates, sulfides, and basic salts.

Of all these components, clay minerals, hydroxides, and organic matter are considered to be the most important group in contributing to and competing for the sorption of trace elements. Blume and Brümmer⁹⁴⁷ described bonding capacity of the main soil components:

- Organic matter fixes: (i) very strongly Cr, Fe, Pb, and Hg, (ii) fairly Cd, Ni, and Co, and (iii) slightly Mn and Zn, and (iii) soil other trace metals.
- Clay mineral fix: (i) very strongly only Fe, (ii) relatively strongly Cd, Co, and Ni, and (iii) rather fairly all other trace metals.
- Oxides/hydroxide (sesquioxides) fix very strongly: (i) Cr, Hg, and Pb, and (ii) relatively strongly all other metals.

Sorption mechanisms can be based on the valency forces and the process is called “chemisorption.” If van der Waals’ forces are involved in the sorption, the process is called “physisorption.” Both sorptions play an important role in the fixation of uncharged complexes. Each trace cation can be sorbed specifically and nonspecifically, as was shown for Cd by Tiller et al.⁷⁹⁶ Pickering¹¹¹⁸ described that cation movement in soils and in weathering substrates can be retarded by a range of interface forces which can be subdivided into categories such as:

- Electrostatic attraction (surface exchange)—ion exchangeable species.
- Weakly adsorbed—attractive forces less well-defined—cations displaceable by reagents such as acetic acid or acidic buffer solution.
- Specifically adsorbed—a chemisorption process in which formal bonding between cation and substrate is strong; sorbate release can require matrix destruction.

The term “adsorption” is commonly used for the processes of sorption of chemical elements from solutions by soil particles. Adsorption is thus the kinetic reaction based on thermodynamic equilibrium rules. At metal equilibrium concentrations, the adsorption by soil particles can be described by either the Langmuir or the Freundlich equations for adsorption isotherms (Bolt and Bruggenwert,⁸⁶ Pierzynski et al., 2005).

The adsorption of trace metal cations by soil particles has been recently studied extensively and free binding energy of these reactions was measured. Wang et al. (2008) reported that these values differ for both soil particles and metals. The adsorption energy is higher for black soil

particles (8.39–9.88 kJ/mol) than for yellow–brown soil particles (5.39–8.54 kJ/mol). Free adsorption energies of trace cations (Cd^{2+} , Cr^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+}) vary within the range of 0.5–2.1 kJ/mol.

Surface charges in soil materials caused primarily by ionic substitutions are exhibited mainly by colloids. White and Zelazny¹⁸³ broadly discussed soil characteristics responsible for charge properties of soil colloids governing all processes of cation exchange, cation selectivity, and ion adsorption. At a low pH, a positively charged surface prevails; while at a high pH, a negatively charged surface develops. The colloids of the majority of soils, therefore, carry negative charges and can be electroneutralized by cations present in the surrounding solutions. In the presence of an excess of cations, the process of exchanging the cations for others maintains the electroneutrality of the system. Thus, the cations adsorbed by the solid phase can be replaced by other cations, most often by H ions. An increase in the stability of adsorbed metals may result from dehydration and recrystallization processes that occur on the surface of the colloids, especially in alkaline soils.

Variable conditions in soil aeration are known as a significant factor in the precipitation of metals. Bloomfield^{946a} carried out a laboratory study on the effect of bacterial sulfate reduction on the accumulation of trace metals in anaerobic sediments. He found that Mo, V, U, Cu, Ni, Zn, Cd, Pb, Co, and to a certain extent Mn were precipitated with FeS during anaerobic incubation. Reoxidation of the sulfidic residue caused the pH decrease and thus Zn, Cd, Pb, Co, and Mn were largely redissolved. Cu and Ni were also mobilized, but Cu was largely fixed by SOM, while Ni was to a lesser extent. The relatively small amounts of Mo, V, and U that dissolved when the suspensions were first aerated were rapidly immobilized as the pH decreased.

The ability of the solid soil phase to exchange cations (the so-called CEC) is one of the most important soil properties governing the cycling of trace elements in soils. The excess amount of adsorbed cations compared to the amount in solution is interpreted as the buffering capacity of soils, while adsorption capacity defines the amount of ions needed to occupy all adsorption sites per unit of mass.

The CEC of different soils varies widely both in quantity and quality and can range from 1 to 100 meq/100 g of soils (this value of most soils does not exceed 30 meq/100 g). High CEC value is reported for SOM (Tan, 1998). Surface properties of soil particulates are the most important factors in defining the capacity for adsorption of microcations. Although total adsorption processes cannot be related simply to CEC phenomena, the adsorbed amounts of cations are in accordance with the CEC. Usually, the solid soil phase with a large surface area, greatly governed by clay minerals (Table 3.11), also shows a high CEC value and high adsorption and buffer capacities.

The affinity of cations for adsorption (e.g., for anionic exchange sites) is closely related to ionic potential (charge/radius). In some systems the metal ions (Zn, Cd, Mn) occupy nearly the same percentages of the CEC of various minerals.⁷⁶³ Some cations, however, may have a higher replacing power than others and can be selectively fixed by the sorbing sites. As Abd-Elfattah and Wada² stated, the selectivity of adsorption reveals a possible formation of the coordination complexes of trace metals with deprotonated OH and COOH groups as ligands. This specific sorption is well-illustrated by trace metals having high affinities for OM and the surface of oxides, with replacing power over alkali and alkaline earth metals. This phenomenon has great importance in the nutrient supply to plants and in soil and ground water contamination.

D SPECIATION

According to the general definition of speciation in the context of soils, sediments and sewage sludge refers to processes of identification and quantification of the different defined species, forms and phases in which an element occurs in investigated materials (Jenny,¹⁰³⁸ Ebdon et al., 2001). However, most often “speciation” also means the description of the amounts and kinds of existing forms of trace elements. Whichever approach is taken, the species, forms or phases are defined: (1) functionally, (2) operationally, and/or (3) as specific chemical compounds or oxidation states.

Trace metals enter the soil layers by a number of pathways, including aerial deposition and by leaching or decomposition of the above-ground parts of plants; by the utilization of wastes and by pesticide and fertilizer application; and by river waters and dredged sediment disposal. The speciation and localization of trace elements in soils are related to their chemistry inherited from parent materials at the time of impactation. Atomic properties also have a significant role in the cation speciation resulting from the formation of ion/ligand complexes (Table 3.7).

As soils consist of heterogeneous mixtures of different organic and organo-mineral substances, clay minerals, oxides of Fe, Al, and Mn, and other solid components as well as a variety of soluble substances, the binding mechanisms for trace metals in soils are manifold and vary with the composition of soils and their physical properties. Thus, a metal may form different species according to whether it is bound to various soil compounds, reacting surfaces, and external or internal binding sites with different bonding energy. In order to assess the speciation or binding forms of trace metals in solid materials, different analytical procedures involving successive extractions have been developed. Considerable controversy has developed over selective extraction methods to determine the amounts of trace metals associated with various soil phases. Despite all the limitations of these methods, some of them have been broadly used.

Lorenz et al.,¹³⁹² however, have stated that the free ionic concentration in soil solution did not better predict concentrations of Cd and Zn in plants than their total concentration in soil solution, which suggests that analysis of Cd and Zn speciation is of little practical importance when their bioavailability is assessed. Tessier et al.¹¹⁶² were among the first to develop the procedure of sequential extraction to determine the speciation of a particular trace metal in soils. Several other kinetic fractionation methods have been developed, and all procedures are based on the assumption that the following species of metals exist in soils:

- Water soluble (e.g., in soil solution)
- Exchangeable
- Organically bound
- Occluded in Fe and Mn oxides
- Definite compounds (e.g., metal carbonates, phosphates, sulfides)
- Structurally bound in silicates and/or other primary minerals (residual fraction)

Depending on the variability in physico-chemical characteristics of metals, their affinity to soil components governs their fractionation. Rule¹⁴⁷¹ broadly reviewed recent literature on phase distribution of trace metals in soils, and concluded that the highest proportions of most metals are found either in residual or in Fe–Mn oxide fractions in both natural and contaminated soils. A high association with exchangeable fraction was observed only for Cd in a few soils. Cd and Zn were also abundant as carbonate fraction in some soils. The association of metals with organic matter was generally lowest for Cd and Ni. Herbert¹³²⁷ found that Cu, Pb, Ni, and Zn are bound primarily to cation exchange sites and organic matter in the reference soil, while in the polluted soils, metal partitioning is dominated by the Fe oxide fractions, despite the high organic matter content.

The soluble plus exchangeable fraction characterizes the mobile species of metals in soils. The other metal fractions are more or less immobile. The mobilization of metals from these fractions, or transformation of mobile to immobile metal species is often a slow process which is strongly controlled by reaction kinetics.⁹⁵⁵ However, a relatively rapid transformation of metals applied in oxide forms to more mobile carbonate species was also observed.¹³⁵⁷

Recent results of several studies presented information on the speciation of trace metals in soils (Salomons and Förstner¹¹³⁷; Tan, 1998; Iskandar, 2001). The distribution patterns of metal species in soils vary widely. For example, in ground water of the forest podzol 58% of the total Cd occurred as CO₃-fixed form, and 38% in mobile ionic forms (Figure 3.7a). In the solution of soil amended with sewage sludge, 95% of the total Cd was present in free cationic form and only 1.7% was associated with organic matter (Figure 3.7b). In light loamy soils, 40% of the total Cd was associated with

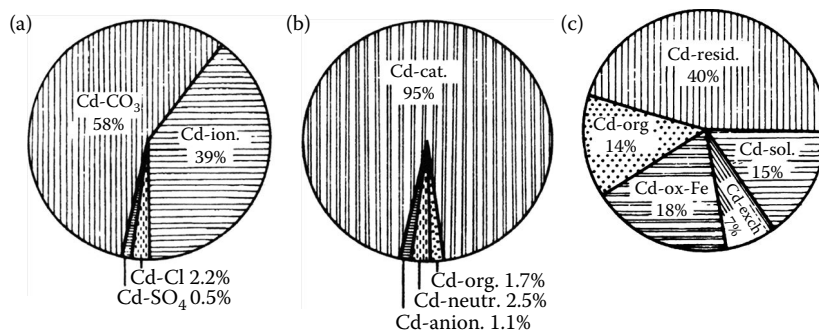


FIGURE 3.7 Relative distribution of Cd species in soils as determined by different methods: (a) in ground water of forest podzol, by GEOCHEM method (Data from Fic, M., Adsorptions—und Desorptions—Verhalten von Cadmium, Chromium, Kupfer und Zink an ausgewählten Böden und Sanden, Ph.D. thesis, Christian-Albrechts-Universität, Kiel, 1987), (b) in solution of soil amended with sewage sludge, by ion exchange procedure (From Alloway, B. J., Tills, A. R., and Morgan, H., *Trace Subst. Environ. Health*, Vol. 18, University of Missouri, Columbia, MO, 187, 1984. With permission), (c) in light loamy soil, by sequential extraction (From Dudka, S. and Chlopecka, A., *Water Air Soil Pollut.*, 51, 153, 1990, Springer Science+Business Media. With permission).

minerals as residual fraction, 18% was bound to hydrous oxides (mainly Fe oxides), 14% was held by organic matter, and only 15% was easily mobile as water-soluble fraction (Figure 3.7c). Han et al. (2007) described effects of land uses on solid-phase distribution on selected trace elements in soils of alluvial plain.

It is still an open question whether, and under which conditions, definite trace metal compounds like carbonates, phosphates, silicates, and others exist in soils. It seems more likely that these metals are bound in soil minerals, for example, Fe and Mn oxides, carbonates, and clay minerals, by isomorphic substitution and by fixation at free structural places. The adsorption capacity of some soil components for cations can be very high and, therefore, a considerable quantity of trace metals can be bound by the adsorption, before the formation of a definite metal compound takes place. Some metals (Cd, Co, Cr, Cu, Pb, Zn), however, are known to form discrete solid phases under specific soil conditions, when they occur in elevated concentrations, and due to diagenetic processes or pollution. Several mineral structures such as $\text{Cu}_2(\text{OH})_2\text{CO}_3$, $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, PbMoO_4 , $\text{Zn}_3(\text{OH})_6(\text{CO}_3)_2$, $\text{Zn}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, ZnFe_2O_4 , and ZnSiO_4 were identified in soils.^{1024,1038} The adsorption-desorption processes can be described by the Freundlich isotherm and calculated with the help of geochemical models like GEOCHEM, proposed by Sposito and Mattigod.¹¹⁵⁴ Although the most important factors that govern these processes are carbonate content (HCO_3^-), CEC, and the Eh-pH system, the adsorption capacity of OM can be of great importance. It has been indicated by the findings of Fic,⁹⁹² who showed a much higher adsorption of Cd, Cr, Cu, and Zn in the acid (pH 2.7) upper horizon of the forest podzol with a high organic carbon content (5.8%) than in the calcareous parent material (pH 8.0).

E TRANSPORT AND BUDGET

The balance input-output budget for trace elements is rarely met, even under natural conditions. The anthropogenic part of this imbalance is related both to the increase of deposition rate of elements and to the decrease in cation leaching, resulting mainly from soil acidification and also from other impaired impacts of the land use. The budgets of metals in forest soils have received much attention, especially in Sweden and West Germany (Table 3.12).

The transport of dissolved trace elements may take place through the soil solution (diffusion) and also with the moving soil solution (mass flow, leaching). Generally, in soils formed under a cool and humid climate, the leaching of trace elements downward through the profiles is greater

than their accumulation, unless there is a high input of these elements into the soils. In warm, dry climates, and also to some extent in humid hot climates, upward translocation of trace elements in the soil profiles is the most common movement. The rates of trace element downward migration are affected by chemical, physical, and biological soil properties, of which the most important are:

- Eh–pH system
- CEC and salt content
- Amount and quality of SOM
- Water and temperature
- Plant species
- Micro- and mezobiota activities

Although much work has been done on trace element movements within soil profiles, complete knowledge concerning their cycling and balances is still lacking. Theoretical reviews of mechanisms involved in the transport and accumulation of soluble soil components were given by Bolt and Bruggenwert⁸⁶ and by Lindsay.⁴⁷⁷ The equilibria discussed by these authors are useful not only in illuminating fundamental reactions that are important in weathering and soil formation but also for use in various fields of agricultural and environmental management. However, the models cannot be used for examining the quality of thermodynamic data obtained from a particular soil without making necessary modifications that take into account the variation of soil properties, and even then, some skepticism may remain. Several detailed studies based on lysimetric experiments, and other research often using isotopic tracers, have yielded much information on element transport. However, each soil profile with developed horizons has its own characteristic trace element movement.

Impoverishment of soils in trace elements is mainly due to their mobility downward with percolating waters through the profiles of freely drained acid soils and also due to trace element uptake by plants. On the other side of the balance is the input of trace elements with atmospheric precipitation and their accumulation in particular soil horizons. In acid soils (e.g., with pH below 6.5), several elements, such as Zn, Mn, Cu, Fe, Co, and B, are easily leached. These elements, however, are likely to form quite stable compounds if the pH of the soil rises above 7. Other elements, such as Mo and Se, are mobilized in alkaline soils, while in acid soils they become almost insoluble.

Trace element budgets have been calculated for forest ecosystem (Table 3.13). Input/output differences show that for the majority of elements, the accumulation rate in the surface soils is positive. However, Fe and Mn, are most likely to be leached down from the surface soil horizon. Leaching rate of trace metals was found to be higher than atmospheric input only in acid sandy soils. Thus, under a forest ecosystem with a high rate of mobility and leaching of metals from the soil, a decrease of these cations is observed, even under a relatively high input. Such a case is described by Mayer and Schultz¹⁰⁸⁸ for the forest ecosystems in Germany.

The calculations of Cd budget for agricultural soils of two European countries (Table 3.14) show that the input of this metal originating both from the point source of pollution and from long-range transport was about equal to the nonpoint source of pollution related to farm management practices. In industrial regions with increased emission of metals, aerial dust and precipitation are the most significant sources of trace metals. It was estimated, that at the global scale the input of most metals is higher from industrial sources than from the application of chemicals and wastes in farming.^{957,1135} The runoff of some chemical elements from agricultural land is observed in the United States (Elrashidi et al., 2007). These authors calculated an annual loss from the watershed, as follows (in g/ha/year): 0.61, Cd; 52, Cu; 21.3, Ni; 1.4, Pb; and 37, Zn.

Kovda¹⁰⁵⁴ made the general assessment of recent soil pollution and calculated the technogenous deposition of trace metals on land to range from 1 to 100 g/ha/year. In soils with a low rate of leaching, the continuous accumulation of trace metals is most likely.

TABLE 3.13
Metal Budgets of Soils of Different Ecosystems (g/ha/year)

Ecosystem, Locality, and Experiment	Element	Total Atmospheric Deposition	Output	Annual Budget
Pine forest, Schwarzwald, Germany ⁹⁰⁷ Brown podzol (seepage water)	Be	0.3	5.6	25.3
	Cd	4.5	1.4	3.1
	Co	5.6	4.3	1.3
	Cu	18	7	11
	Ni	34	17	17
	Mn	70	430	2360
	Pb	110	6	104
	Zn	210	76	134
	Fe	300	2000	21,700
Birch and spruce forest, Solling Mountains, Germany ³¹⁰ Brown acid silty loam (seepage water)	Bi	0.4	0.2	0.2
	Hg	0.4	0.2	0.2
	Tl	1.2	0.3	0.9
	Sb	3	0.3	2.7
	Cd	13	9	4
	Ni	15	14	1
	Cr	22	2	20
	Mn	200	6300	26,100
	Cu	224	108	116
	Zn	3900	1900	2000
	Fe	1600	1900	2300
	Cd	2	5	23
	Cr	8	10	22
Spruce forest, Hässleholm, Southern Sweden ^{815,816} Podzolic forest soil (lysimeter)	Ni	10	9	1
	V	12	28	216
	Cu	20	29	29
	Pb	150	81	69
	Zn	180	270	290
	Fe	2000	13,000	211,000
	Cd	3.2	4.2	21
Spruce forest, Gårdsjön, Sweden ⁹⁴⁰ Sandy shallow soil (lysimeter)	Cr	3	8.3	25.3
	Cu	9	4.8	4.2
	Ni	5.7	21.3	216
	Pb	77	2	75
	Mn	90	690	2600
	Zn	331	461	2130
	Fe	1500	1400	100

Bergkvist et al.⁹⁴² reviewed recent literature on trace metal fluxes in forest ecosystems with an emphasis on metal budgets in both forest ecosystems and forest soils. Their final conclusions can be summarized as follows:

- The rate of both soil acidification and metal leaching depends greatly on the soil type and vegetation type.
- The organic topsoil (litter and mor layers) is the most significant sink for trace metals, especially for Cu, Pb, and Cr; but when organic compounds mobilize these metals, they are likely to precipitate in the upper B horizon.

TABLE 3.14
Balance of Cadmium in Agricultural Soils of Poland and Germany (g/ha/ year)

	Poland	Germany
Input		
Fertilizers	1–2.5	1–6
Slurry	2.5	—
Sludges	1.5	1–25
Harvest residues (recycling)	3	0.3–8
Atmospheric input	2.5–4	3–8
Total input	10.5–13.5	4.3–47
Output		
With crops	3	1–5
With seepage water	3	1–2
Total output	6	2–7
Balance (net gain)	4.5–7.5	1.3–40

Source: Adapted from Brümmer, G. W., in *The Importance of Chemical Speciation in Environmental Processes*, Bernhard, M., Brinckman, F. E., and Sadler, P., eds., Dahlem Konferenzen, Springer-Verlag, Berlin, 169, 1986 and Kabata-Pendias, A., *Heavy metal concentrations in arable soils of Poland*, Pamiet, Pulawski, 74, 101, 1981 (Po).

TABLE 3.15
Balance of Cadmium, Copper, and Zinc in Arable Land in the Netherlands, Calculated for 2003 (in 10³ kg)^a

Input/Output	Cd	Cu	Zn
Input			
Animal manure	3	425	1250
Mineral fertilizers	1	35	50
Deposition	1	20	80
Other sources	0	15	140
Total input	5	495	1520
Total output	3	95	560
Balance (net gain)	2	400	960

^a After Dach J., Starmans D. 2005. *Agric. Ecosystems Environ.* 107:309–316.

- The relationship between the pH and the total concentrations of Zn, Cd, and Ni is very close although nonlinear; a drastic change in the metal solubility in the mineral soil (or horizon) occurs in the pH range of 4.0–4.5.

Calculated balance for Cd, Cu, and Zn in arable land in the Netherlands for 2003 (Table 3.15) showed a lower yearly accumulation of these metals than in 1980. Rühling and Tyler (2004) calculated recent changes in the atmospheric deposition of 60 elements in South Sweden. They stated that improved emission control in all industrial technologies resulted in decreases of aerial deposition of all elements and especially of Pb. The median concentration of all investigated elements in moss (pleurocarpic mosses) was 2.7 times higher in 1975 than in 2000.

4 Soil Constituents

I INTRODUCTION

Quantitatively, trace elements are negligible chemical constituents of soils, but are essential as micro-nutrients for plants. The first publications on trace elements were devoted to plant nutrition problems. Further, it was recognized that the behavior of trace elements in the soil differs widely for both the element and the soil and that these differences should be understood better for the prediction and effective management of the trace element status of soils. Although trace elements are mainly inherited from the parent rocks, their distribution within the soil profiles and their partitioning between the soil components reflect various pedogenic processes as well as the impact of external, especially anthropogenic factors (e.g., agricultural practices, industrial pollution). Recently, trace element contents, forms, and behavior are significant information to soil survey users (Wilson et al., 2008).

Trace element associations with the particular soil phase and soil component appear to be fundamental in defining their behavior. The trace element composition of soils is relatively well-established (Figure 4.1), although there are still diversities in analytical results, especially in the measurements of very small quantities. Currently, there is also a great deal of work on the distribution of these elements among soil components. One must realize, however, that present-day techniques for soil fractionation are quite drastic and cannot provide very comparative and representative results. Knowledge of the behavior and reactions of separate soil components with trace elements, although fundamental, should not be related directly to overall soil properties, and great caution is needed in using several theoretical models for predicting the behavior of trace elements in soils.

II TRACE ELEMENTS

On the basis of the results of numerous studies, investigations, and observations, the main soil parameters that govern processes of sorption and desorption of trace elements are presented as follows:

- pH and Eh values
- Cation exchange capacity (CEC)
- Fine granulometric fraction (<0.02 mm)
- Organic matter
- Oxides and hydroxides, mainly Fe, Mn, and Al
- Microorganisms

Trace element concentrations significantly differ among both soil groups and geographic regions (Sumner, 2000). This statement indicates that parent material and climatic conditions have predominated impact on the trace elements status of soils. Several soil variables control trace element contents and behavior in soil. A factor of soil parameters was established by Kabata-Pendias and Krakowiak¹³⁵⁶ based on the calculation of correlation coefficient matrices for metals and some soil parameters such as: pH, clay fraction content, CEC, SOM, and Fe content. For about a thousand soil samples, the strongest linear positive correlation was obtained for the metals and fine soil

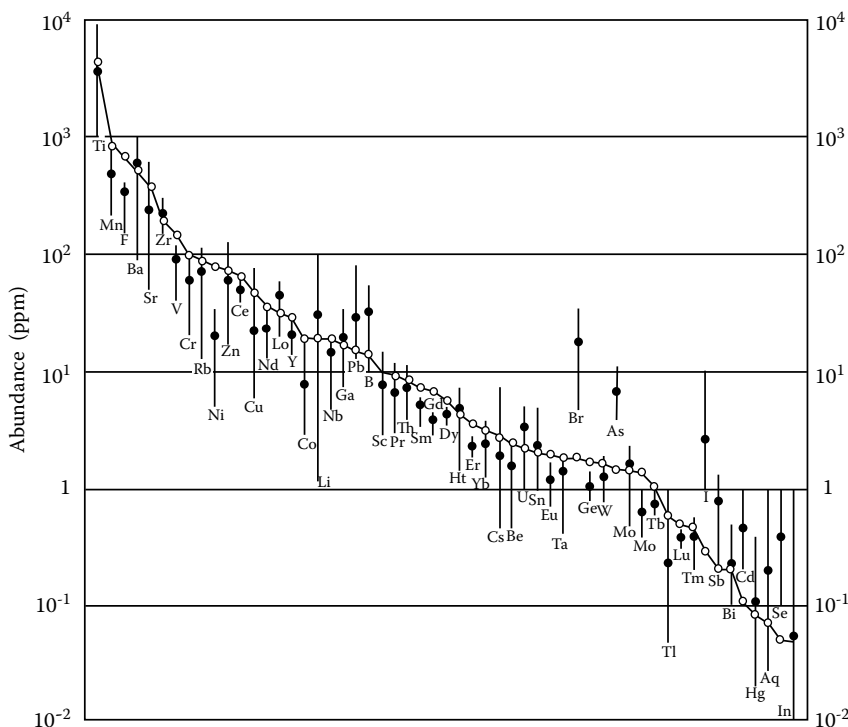


FIGURE 4.1 Trace elements in soils compared to their abundance in the lithosphere. Open circles mean content in the lithosphere; black circles mean content in topsoils; vertical lines mean values commonly found in topsoils.

granulometric fraction. This relation varies, however, for given metals, and is well illustrated by increasing mean content of trace metals in soils with increasing content of clay fraction (Table 4.1). The highest relative explanation index (60–75%) was calculated for Zn, Fe, Ni, and Cr, whereas the lowest explanation (10–30%) was for Cd, Pb, Cu, and Mn (Figure 4.2). A similar trend in correlation of metal contents with CEC of soil was observed, but at much smaller relative explanation. A high explanation (>60%) was obtained for Ni versus Fe in soils, while this relation was very low (<20%) for Cd and Cu (Figure 4.3). SOM influences the distribution of most metals, but only at about 15% of the relative explanation. The smallest relationship with SOM (<10%) was observed for Cd and Mn. Owing to the strongest association of trace metals with clay soil fraction, the calculated range of metals based on the content of soil clay fraction gives acceptable values for the estimation of background contents of metals (see Chapter 2, Section 2.4.1). The positive correlation of trace metals (Co, Cu, Ni, Pb, and Zn) with clay content of soils is, according to Lee et al.,¹³⁸⁶ responsible for increasing their levels in the B soil horizons where clay is translocated from the A soil horizon. Elpatevsky et al.,¹²⁹⁰ and Gao et al.,¹³⁰⁵ on the contrary, stated that the main factor of trace metal migration is DOM. Based on *in situ* determination of partitioning coefficients (K_p values), Janssen et al.,¹³⁴⁵ concluded that, pH and amorphous Fe content are the most influential factors in the partitioning of metals in soil. The impact of contents of Fe, Mn, Al, silt, clay, and CEC value on the phytoavailability of trace metals is significant and affects the broad range of values of tolerant limits (TL), as follows (in mg/kg): Cd, 1–4; Co, 3–44; Cr, 41–131; Ni, 10–92; Pb, 4–154; and Zn, 13–149 (Fadigas et al., 2006).

Interactions between elements in soils are of multivariant character but may be mainly attributed to the sorption sites of soil particles and also to the surface root cells and to root exudates. Most commonly these are mainly impacts of SOM/DOM and major elements on the distributions and

TABLE 4.1

Arithmetic (A) and Geometric (G) Mean Contents of Trace Metals (mg/kg) and Iron (%) in Soils of Various Textural Groups in Poland

Metal	Light Sandy (N = 552)		Medium Loamy (N = 168)		Heavy Loamy (N = 100)	
	A	G	A	G	A	G
Cd	0.29	0.22	0.35	0.31	0.86	0.51
Cu	10.4	7.2	13.2	11.8	20.3	18.5
Cr	8.0	7.0	15.3	14.6	25.6	24.3
Mn	254	205	399	368	640	574
Ni	5.5	4.8	11.8	10.9	23.4	21.5
Pb	14.2	12.6	17.7	16.4	25.2	20.9
Zn	41.7	32.5	59.7	51.5	91.0	79.5
Fe (%)	0.6	0.5	1.2	1.1	2.0	1.9
Be	0.30	0.26	0.55	0.49	0.79	0.73
Co	3.5	2.8	6.0	5.4	9.1	8.5
La	8.4	7.6	14.7	14.2	19.2	18.4
Li	4.8	4.0	9.6	8.5	17.3	15.4
Mo	1.1	0.2	1.4	0.3	2.0	0.4
Sr	11	10	20	17	30	24

Source: Adapted from Kabata-Pendias, A. and Pendias, H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 400, 1999 (Po).

forms of some trace elements in soils. The main interactions (or relationships) in soils, often associated with microbiota, are:

- Ca: B, Ba, Cd, Co, Cr, Cs, Li, Mn, Ni, Pb, Sr, and Zn.
- P: As, Cr, Hg, Mo, Mn, Ni, Pb, Rb, Se, and Zn.
- Fe: Co, Ni, Mn, Mo, Cr, and Zn.
- Mg: Cr, Mn, Zn, Ni, Co, and Cu.
- Mn: As, Cr, Cu, Mo, Ni, V, and Zn.
- Cu: Mo.
- Zn: Cd.

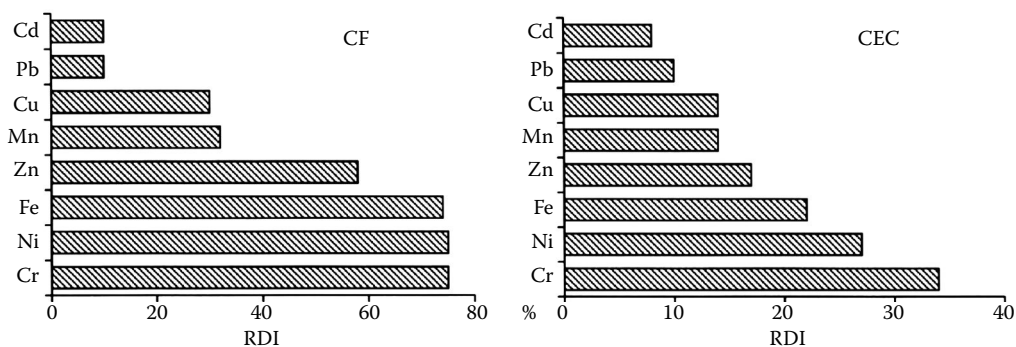


FIGURE 4.2 Relative explanation index (RDI) of statistically significant relationship between trace metals and content of clay fraction, <0.02 mm (CF) and CEC in mineral soils at the 99% confidence level.

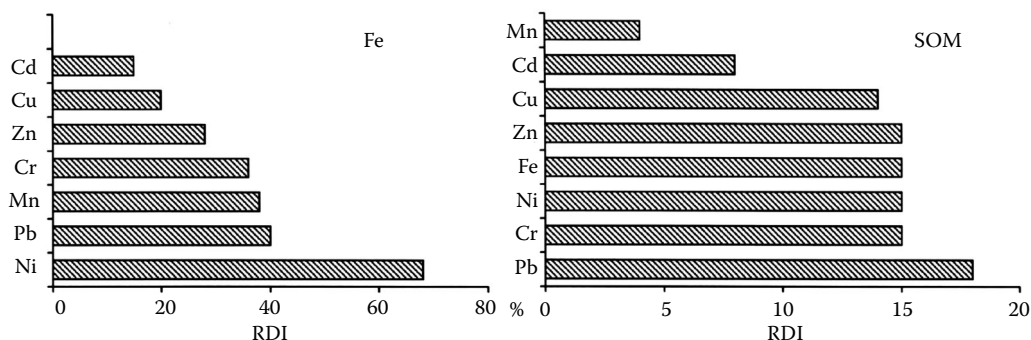


FIGURE 4.3 RDI of statistically significant relationship between trace metals and Fe content, and SOM of mineral soils at the 99% confidence level.

The occurrence of trace elements in soil materials from natural as well as from contaminated sites shows great variability in both the horizontal and vertical dimensions. The heterogeneity of soils, especially at the microscale, creates real problems in representative sampling that have serious impacts on the reproducibility and comparability of analytical data. This is of great concern in the assessment of background (pristine) contents of trace elements in soils. World-soil average contents of trace elements may serve, to some extent, as background values (Table 3.2). Although a real pristine status of trace elements in soils does not exist nowadays, even in remote regions, some values of trace elements in “uncontaminated” soils are prerequisites as reference values for the evaluation of soil pollution. Several methods were developed to calculate background contents of trace elements in soil (see Chapter 2, Section 2.4.1).

III MINERALS

The mineral constituents of soils inherited from the parent rocks have been exposed for various periods of time to weathering and pedogenic processes. The soil–mineral system, which is not necessarily in equilibrium with the soil solution, is complicated by the processes of degradation and neoformation of minerals, as well as by mineral reactions with organic compounds.

The common primary minerals in soils inherited from the parent material can be arranged in two parallel series, according to their susceptibility to weathering processes: (1) series of felsic minerals: plagioclases > K/Na-feldspars > muscovite > quartz, and (2) series of mafic minerals: olivine > pyroxenes > amphiboles > biotite. These series are based on broad generalizations, and many exceptions may occur in particular soil environments. The primary minerals occurring in some soils are mostly of a larger dimension and are not involved in the sorption processes. They are, however, considered to be the source of certain micronutrient elements. Several secondary minerals are formed in soils or are inherited from parent materials: goethite, hematite, gibbsite, dolomite, calcite, gypsum, and clay minerals.

The approximate composition of mineral constituents of surface soils presented in Figure 3.2 shows that quartz is the most common mineral in the soils, constituting 50 to more than 90% of the solid soil phase. Even in geochemical conditions favorable for the leaching of silicates, quartz remains as a basic soil mineral. Feldspars are of low relative resistance to weathering in soil environments and their alteration usually provides materials for clay mineral formation. Carbonates (calcite, dolomite) and metal oxides/hydroxides are usually accessory minerals in soils of humid climatic zones, while in soils of arid climatic zones they may be significant soil constituents.

The size and shape of mineral particles determine their ratio of surface to volume and mass, and this ratio determines their physical and chemical properties. Therefore, the grain-size composition of soils is considered to be one of the most important factors in soil characteristics and is included in the systems of soil evaluation and classification.

Sorption properties of the mineral part of soil material are associated principally with the clay and silt-size fractions. These fractions are mixtures of several aluminosilicate clay minerals with lesser amounts of quartz, feldspars, and various oxides and hydroxides. In certain soils, carbonate and phosphate minerals are present, and in others, such minerals as sulfides and sulfates may occur.

A CLAY MINERALS AND OTHER ALUMINOSILICATES

The boundaries of the mineral group described as “clay minerals” are not well defined, and they tend to enlarge with increasing knowledge. They also are called phyllosilicates (sheet silicates). The division of minerals in this chapter does not relate to any classification system. The common clay minerals in soils can be subdivided into four groups:

- Kaolin (kaolinite, halloysite, dickite, nacrite)
- Smectite (montmorillonite, nontronite)
- Illite (including weathered mica-vermiculite)
- Chlorite (including similar minerals with variable chemical composition)

Each group includes many compositional and structural varieties; however, they are all 1:1 or 2:1 layer-type aluminosilicates. Clay minerals also are called phyllosilicates (sheet silicates). The structure and chemistry of these minerals have been extensively described in many monographs.^{49,281} The surface properties of minerals (high active surface areas and presence of an electrical charge) seem to be fundamental for the buffer and sink properties of soils, and therefore have a major effect on chemical and physical soil properties. The bonding processes for absorbed microcations, although carefully studied, remain controversial.^{2,227,356} It has been well-demonstrated, however, that equilibrium, and pH and Eh values are the most basic qualities in the reactions of sorption and release of microcations by clay minerals.

Poorly crystalline clay minerals (some time amorphous aluminosilicates), such as allophane and imogolite may form very complex and relatively stable association with OM in soil (Wada, 1989). Clays containing exchangeable transition cations (such as Cu, Fe, and Co) are known to act as electron or proton acceptors, thus they can be activators in transformations, decomposition, and polymerization of the adsorbed organic species. Allophanes are present in many soils, and the investigators pointed out their importance in the formation and transformation of noncrystalline clay materials and opaline silica.⁸³³ Both allophane and imogolite make sequences of various types and are formed mainly in the soils developed under a warm humid climate. Allophanes are more stable in acid soils, and imogolite is more stable in neutral and alkaline soils. Very often they occur as “gel films” that coat soil particles. The effect of these inorganic coatings may be diverse, both increasing and decreasing trace element sorption; they may also reduce the biological availability of occluded trace elements.³⁵⁶ Thin films of inorganic and/or organic materials coated soil particles may significantly alter interfacial reactions and thus control sorption processes (Bertsch and Seaman, 1999). Fine soil fractions associated with humus molecules of the gel structure reveal increased sorption capacity for trace metals (Fedotov et al., 2008).

Clay minerals may contain negligible amounts of trace elements as structural components, but their sorption capacities to trace elements play the most important role. The affinity of trace ions for the clay surface has been examined by many investigators; and while many aspects have been clarified, still much remains to be learned about the adsorption processes. Hardy and Cornu (2006) stated concisely that TE contents increases as particle-size decreases. Surface area of soil minerals/materials is measured using various sophisticated methods and for different elements and compounds. Surface area measured for N₂ varies (in m²/g) from 0.5 for uncoated goethite/feryoxhite coated sand to 99 for smectite (Sparks, 1999).

Clay minerals vary in chemical composition and thus their properties, and especially CEC values differ (Table 3.11). The CEC values vary with the type of clay in the following sequence: montmorillonite, imogolite > vermiculite > illite, chlorite > halloysite > kaolinite. Amounts and

TABLE 4.2
Surface Area of Various Soils

Granulometric Composition of Soil	Surface Area (m ² /g)	
	Ahlrichs ⁵	Dobrzański et al. ¹⁸²
Clay and loam	150–250	22–269
Silty loam	120–200	24–117
Sandy loam	10–40	4–67
Silt and clay	—	17–167

kinds of clay minerals (mainly in fine granulometric soil fraction) are responsible for values of the specific surface area of soil materials (Table 4.2). The ability of the clays to bind the metal ions is correlated with their CEC, and usually the greater the CEC, the greater the amount of cation adsorbed.

The minerals of the montmorillonite group can expand and contract in response to charge and size of the absorbed cation between the clay platelets. Thus, their sorption capacity will differ when saturated with different cations. The microcations sorbed by montmorillonite are also easily released into the liquid phase and, therefore, can be an important pool of micronutrient supply to plants growing in particular soil conditions.

Relatively little is known about the adsorption of metal ions on amorphous alumina and silica gels. The mechanisms of coprecipitation and mobilization of certain trace cations with alumina or silica gels may play a significant role in their behavior in the particular soil, especially in those of the tropical climate zone. There are suggestions that metal ions (mainly Cu²⁺) can substitute for aluminum in the mineral structures, while soluble silicic acid promotes adsorption of Co, Ni, and Zn by clays.^{517,793} The strong adsorption of divalent trace cations (Cu, Pb, Zn, Ni, Co, Cd, and Sr) by freshly precipitated alumina gel is suggested by Kinniburgh et al.³⁹² to play a role in determining the availability to plants and the movement of some of these cations through the soil.

Some aluminosilicates are known to occur in soils as phyllosilicates (palygorskite, attapulgite, sepiolite) and as zeolites. They all have alternative 2:1-type open structures and are associated with the clay minerals. They can be inherited from parent materials, but can also be of pedogenic origin.⁹⁰¹ Most often, these minerals were found in neutral or alkaline soil series, especially in the presence of salts (e.g., Solonetz, Solonchaks, Andosols, Calcisols). Some of them are more acid resistant than others in the soil environment. However, the detection of these minerals, especially zeolites, can be questioned due to possible destruction during chemical pretreatments of soil material.

Zeolites (aluminosilicates with microporous structure) occur in a wide variety (48 naturally and >150 synthesized) and exhibit a high affinity to sorb ions, gases, and liquids. They are active in the sorption of both cations and anions.⁴⁹ Zeolites are widely used as ion exchange in soil remediation, water purification, and so on.

All of clay amorphous aluminosilicates have relatively high CEC values and a great affinity to react with soil organic compounds. Under normal soil conditions, they are important trace element sinks.

B OXIDES AND HYDROXIDES

Several oxide minerals, such as silicon oxides, titanium oxides, aluminum oxides, and hydroxides occur in soils. They are formed during weathering of primary minerals as well due to other pedogenic processes. Soil pH and soil redox status (Eh) govern all oxidation–reduction reactions in soil. Some oxides, for example, Fe³⁺ and Mn⁴⁺, may easily change their oxidation state under suboxic condition and form Fe²⁺ and Mn²⁺.

Biogenic synthesis of some oxides is also reported (Tebo et al., 2004). Usually they have a high surface area (up to 800 m²/g) and therefore a high affinity for ion absorption. The oxidation of organic matter is involved in redox soil processes and has an impact on the ion oxidation state (Chadwick and Chorover, 2001).

In relation to trace element behavior, the most important are Fe and Mn oxides/hydroxides. Aluminum hydroxides can adsorb a variety of trace elements and in some soils the role of these oxides can be more important than that of Fe oxides in retaining certain trace elements. As Norrish⁵⁷⁰ has stated, however, there is little direct evidence to support this view.

The Fe and Mn oxides occur in soils as coatings on soil particles, as fillings in cracks and veins, and as concretions or nodules. Nodules are generally formed in soils with fluctuating oxidation–reduction regimes. Their composition is variable, but is always highly enriched in Fe and Mn. Norrish⁵⁷⁰ and Hiller et al.,¹⁰²⁵ indicated that many trace elements in soils are concentrated along the deposited oxides in soil material. Fe and Mn oxides have a high sorption capacity, particularly for trace elements, of which large amounts can be accumulated in nodules and at Fe- and Mn-rich points (Table 4.3). The mechanisms of sorption involve the isomorphic substitution of divalent or trivalent cations for Fe and Mn ions, the cation exchange reactions, and the oxidation effects at the surface of the oxide precipitates. Brümmer et al.⁹⁵⁵ studied reaction kinetics of the sorption of trace metals by goethite and stated that these processes involve: (1) adsorption of metals on external surfaces, (2) solid-state diffusion of metals, and (3) metal binding and fixation at positions inside the mineral particles.

Oxides/hydroxides of Fe and Mn are relatively common constituents in soils and, having a high pigment power (mainly Fe oxides), determine the color of many soils. Fe and Mn oxides are present in soils in various mineral forms as well as in crystalline, microcrystalline, and amorphous forms. Their structure and chemical properties are well-described by several authors (Hem,³¹³ Jenne,³⁵⁶ McKenzie,^{524,526} and Schwertmann and Taylor⁶⁹⁹). Although several minerals of the Fe oxides have been detected in soils, goethite is claimed to be the most frequently occurring form. Norrish⁵⁷⁰ reported that simple oxides and hydroxides of manganese do not occur in soils and that the most common mineral forms are lithiophorite and birnessite. Chukhrov et al.,¹⁴⁰ on the contrary, have identified vernadite, a simple hydrous oxide of Mn (of complex composition with associated cations), as the most frequent form in the majority of soils.

Ferromanganese coatings on quartz grains are often composed of ferrihydrite and vernadite. Therefore, the sorption of cations depend on the sorbate compound (Manceau et al., 2007). Vodianizkii (2006) studied the structure of Fe/Mn nodules and found that As, Cr, and Ni reveal an affinity to Fe-hydroxides; Cd, Co, Cu, and Ni, to Mn-oxides; and Zn is most likely to bind to phyllosilicates (sheet silicates). Timofeeva (2008) reported that Fe/Mn nodules accumulate intensively Co, Mn, Ni, and Pb, and to a lesser extent Cu and Mo. Trace element concentrations in nodules highly differ depending on thle size and valence states and is associated with Fe and Mn contents. Aide (2005) described that relationships of Fe with trace metals is relatively close, and decreases in the following order: V > Cr > Pb > As > Se. The relationship with Mn content of nodules and trace elements is less pronounced and is observed mainly for Co and Ce.

The Fe/Mn oxides are exposed to reduction and chelation solubility and oxidation–precipitation reactions, in which microbiological processes play an important role. Redox processes, in particular, in marsh soils result in the formation of concretions with dominating Fe and Mn accumulation.¹⁰²⁵ Different nodules of Fe and Mn are known to originate from both chemical and microbial processes; also, the formation of some crystalline minerals is known to be affected by microorganisms. The most common Fe-oxidizing bacteria (*Thiobacillum*) and Mn-oxidizing bacteria (*Metallogenium*) are able to tolerate high concentrations of several trace metals (Zn, Ni, Cu, Co, and Mn). Thus, they are also involved in trace metal cycling in soils.

Variable charges at the surfaces (mainly of Fe oxides) also promote the adsorption of anions. A high sorption capacity of Fe oxides for phosphates, molybdates, and selenites is most widely observed and is highly pH dependent, being lower at high pH values.⁶³⁸ Trace element sorption by the oxide surface is a highly pH-dependent process of cation and oxyanion adsorptions (Basta et al.,

TABLE 4.3
Trace Elements in Iron and Manganese Oxides

	Fe-Rich Soil Nodules (977) ^a	Fe-Rich Points of Surface Soils (570)	Goethites (570, 881)	Fe-Si- Rich	Fe-Mn- Rich (1025)	Ti-Fe- Rich	Mn-Rich Points of Surface Soils (570)	Manganese Nodules			Manganese Minerals	
								(94)	(524)	(977) ^a	From Soils ^b (525)	From Deposits ^c (837)
%												
Fe	40.1	7.97–29.65	51.7–61.9	6–28	2–15	18–29	3.92–17.69	0.016	—	2.3	0.65–4.6	0.1–4.5
Mn	3.4	0.07–1.52	0.26–0.5	5	16–40	0.3–5.5	5.5–13.6	16	0.36–7.2	50.3	47.4–59.9	28–61
Ti	0.13	—	—	—	—	31–39	—	—	—	0.02	—	—
mg/kg												
Ba	890–1790	—	—	—	—	—	5730–28,640	2000	140–2300	—	32,000–54,000	110,000–128,000
Cd	—	—	—	20–430	90–520	70–740	—	8	—	—	—	—
Ce	—	—	—	—	—	—	—	720	—	—	—	—
Co	300	400–700	80 ^d	40–830	70–390	100–110	5400–24,400	3000	82–380	—	4500–12,000	140–12,000
Cr	—	—	1000 ^d	—	—	—	—	14	30–120	—	—	—
Cu	100	40–720	800	50–980	80–450	150–1110	390–960	2600	—	200	—	130–12,600
I	—	—	—	—	—	—	—	120–900	—	800	—	—
Li	—	—	—	—	—	—	—	—	—	—	300–700	2–5340
Mo	—	—	850	—	—	—	—	410	—	—	—	—
Ni	100	260–630	170 ^d	40–680	80–680	40–640	860–4870	4900	39–67	600	1000–3400	120–10,900
Pb	—	460–1390	—	130–5690	120–11,910	160–2720	2600–20,400	870	34–100	—	—	—
V	400	—	17,000	—	—	—	—	440	88–110	100	—	—
Zn	400	720–2570	17,300– 23,500	50–1790	350–1800	30–1580	320–5540	710	30–33	3500	—	50–3800

Note: References are in parentheses.

^a Mean contents.

^b Identified minerals: lithiophonite, birnessite, and hollandite.

^c Identified minerals: psilomelane, cryptomelane, lithiophonite, and pyrolusite.

^d In magnetite separated from soils (ignited weight).

2005). The amount of a particular ion that is adsorbed depends mainly on the pH of the equilibrium solution. The maximum adsorption values for various ions on Fe oxides range between pH 4 and 5.⁶⁹⁹ However, their sorption capacity increases significantly with increasing pH of media and was found to be the highest at 8 pH (Sparks, 1999).

Some investigators give the order of preferential sorption of metals by goethite as $\text{Cu} > \text{Zn} > \text{Co} > \text{Pb} > \text{Mn}$,⁶⁹⁹ while others presented metal ion affinities for the oxide surface in the following orders: $\text{Cu} > \text{Pb} > \text{Zn} > \text{Co} > \text{Cd}$, and $\text{Pb} > \text{Zn} > \text{Cd} > \text{Tl}$.^{240,252} However, the extrapolation of these results to all soils is difficult. Apparently, hydrous oxides of Fe and Mn are the most important compounds in the sorption of trace metallic pollutants, and they exhibit diverse affinities to cations having approximately the same physical dimensions as Mn^{2+} , Mn^{3+} , Fe^{2+} , and Fe^{3+} ; which are Co^+ , Co^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{4+} , and Ag^+ .

C CARBONATES

Calcium is a relatively common constituent of several soil minerals. However, only calcite [CaCO_3], dolomite [$\text{CaMg}(\text{CO}_3)_2$], and gypsum [$\text{CaSO}_4 \cdot \text{H}_2\text{O}$] are the main source of this element. Calcite is the most widespread and relatively mobile form of Ca carbonates present in soils; it is usually greatly dispersed and has a major influence on the pH of soils and therefore on trace element behavior. Carbonates of Ca and Mg are inherited mainly from limestones, but may also form in soils, under specific conditions (neof ormation processes).

Carbonates present in soils are often in metastable and polymorphic varieties and thus sensitive to drainage conditions. Carbonates are common constituents in the soils where evapo-transpiration potential exceeds the rainfall. On the contrary, in soils with a high rate of percolating water, carbonates are easily dissolved and leached out. Nevertheless, Ca is usually the predominating cation in solutions of almost all soils.

Trace elements may coprecipitate with carbonates, being incorporated in their structure, or may be sorbed by oxides (mainly Fe and Mn) that were precipitated onto the carbonates or other soil particles. Metallic ions may also influence processes of carbonate precipitations.³⁵⁶ The greatest affinity for reaction with carbonates has been observed for Co, Cd, Cu, Fe, Mn, Ni, Pb, Sr, U, and Zn. These processes are commonly observed in metal-contaminated soils. A wide variety of the elements under various p edochemical environments may substitute for Ca in different proportions in nodular calcites. As Vochten and Geyes⁸²⁸ observed, the secondary calcite crystals show a remarkably high content of Sr and Co—up to 1000 mg/kg concentrations. Sorption properties of hydroxyapatite (HAP) toward Pb^{2+} are stronger than toward Cd^{2+} , Zn^{2+} , and Sr^{2+} . Smiciklas et al. (2008) reported that HAP is involved in the main operating mechanism for Pb immobilization.

Carbonates can be the dominant trace element sink in a particular soil, but the most important mechanisms for regulating the trace element behavior by carbonates are related to the variation of soil pH. For example, CdCO_3 , $\text{Cu}_2(\text{OH})_2\text{CO}_3$, and $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and are likely to occur in neutral or alkaline soils polluted with these metals.^{1038,1046}

D PHOSPHATES

Crystalline forms of phosphate minerals rarely occur in soils; however, many varieties of metastable and metamorphous phosphates are of importance in pedogenic processes. There are few data on the occurrence of Ca phosphates (apatite and hydroapatite) or other phosphates in soils. Rather, it has been suggested that an intimate mixture of Ca, Fe, and Al phosphates predominate in soils.³⁵⁶

Phosphate rocks are the only source of P in agriculture, for example, for plant production. Global mining of phosphate rocks increased dramatically during the last half-century to meet the demand of agriculture, and partly production of chemicals (detergents).

Phosphate rocks contain variable, and often elevated, amounts of trace elements (Table 4.4), depending on the source of phosphate ores. Of greatest concern is increased level of potentially

toxic metals (PTMs), and in particular F, U, Th, and some radionuclides (Po, Rn) (Glasser and Jones, 2008).

The most abundant phosphates are apatite group minerals. Some substitutions for Ca by trace elements are known to occur in natural apatites; they are, however, of little importance in soils. Many trace elements (Ba, Bi, Cu, Li, Mn, Pb, Re, Sr, Th, U, and Zn) can be incorporated, together with Fe^{3+} , and Al^{3+} , in hydrated phosphates.⁸⁰⁹ Norrish⁵⁷⁰ reported extremely high concentrations of lead (1–35% PbO) in the phosphate concentrates occurring in ferralsols (lateritic podzolic soils). At the range from neutral to alkaline reactions, a possible formation of Pb phosphates in Pb-polluted soils is reported.^{1038,1046} According to Cao et al. (2004), phosphate rock has the highest affinity for Pb and the greatest stability of this metal is due to the formation of fluoropyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2]$.

TABLE 4.4
Trace Elements in Phosphorites and Phosphate Fertilizers (mg/kg)

Element	Phosphate Rocks (98, 809, 1418, 1558)	Phosphate Fertilizers (381, 554, 1362)
Ag	—	0.8–3
As	0.4–188	2–1200
B	3–50	5–115
Ba	1–1000	200
Be	0.5–10	—
Br	—	10–500
Cd	0.01–0.100	7–170
Ce	9–100	20
Co	0.6–12	1–12
Cr	2–1600	66–600
Cu	0.6–394	1–300
F	31,000	8500–38,000
Hg	0.2–1000	0.01–0.12
I	0.2–280	—
La	7–130	60–100
Li	1–10	—
Mn	1–10,000	40–2000
Mo	0.03–138	0.1–60
Nb	—	20–570
Ni	0.2–1000	7–32
Pb	1–1000	7–225
Rb	—	90–200
Sb	0.2–10	—
Se	1–10	0.5–25
Sn	0.2–15	3–19
Sr	1000–2000	25–500
Ti	100–3000	—
U	8–1300	10–800
V	20–5000	2–180
Y	—	30–180
Yb	—	8–14
Zn	4–345	50–1450
Zr	10–800	50–1560

Note: References are given within parentheses.

Other trace metals are also readily adsorbed by phosphate rocks and therefore several experiments have been conducted on the immobilization of trace metals by phosphate rocks and/or phosphate materials (Campbell et al., 2006; Illera et al., 2003; Hettiarachchi et al., 2001). On the contrary, there is a growing awareness on the transfer of nonmobile to bioavailable forms of some trace elements, and in particular of U and radionuclides, under various soil conditions. Especially phosphogypsum wastes used in soil amendments are significant sources of several PTMs (Pérez-López et al., 2007).

E SULFIDES, SULFATES, AND CHLORIDES

Sulfides are negligible compounds in soils that develop in a humid climate. However, in acid sulfate soils developed in tropical climatic zones (especially in waterlogged environments), in soils in the *Anoxic* and *Sulfidic* categories they are likely to occur. Under these conditions, bacteria (e.g., *Thiobacillus ferrooxidans*) form Fe sulfides (e.g., pyrite, FeS_2). Also other metallic ions (mainly Fe^{2+} , Mn^{2+} , Hg^{2+} , and Cu^{2+}) may form relatively stable sulfides of acidic or neutral reducing potential in flooded soils. Several other trace metals (Cd, Co, Ni, Sn, Ti, and Zn) can also be easily coprecipitated with iron sulfides.^{356,828} The precipitation of metallic ions as sulfides is an important mechanism for regulating the solution concentration of both S^{2-} and metallic cations. Sulfides of trace metals may be transformed into more soluble oxidized sulfates when flooded soil becomes drained and aerated. Pyrite is the most common mineral of Fe sulfides in soils and other geochemical environments. Some other trace metals which readily form sulfides may also be, as is Fe, remarkably related to microbial S cycling in soils, as was described by Trudinger and Swaine.⁸⁰⁹ When sulfide soils are drained and exposed to air, the sulfides react with oxygen and form sulfuric acid. Acid sulfide soils are widespread around wetland coastal regions. Increased mobility of Cd and Ni in acid sulfate soils on the coastal plains of Finland is of environmental concern (Sundström and Aström, 2006).

Sulfates of trace metals are not common in soils, especially in soils with good drainage. Sulfates of metals, mainly of Fe (e.g., jarosite [$\text{PbFe}_3(\text{OH})_6(\text{SO}_4)_2$]), but also of Al (alunites) and Ca (gypsum, anhydrite), are likely to occur under oxidizing soil conditions. They are readily soluble and therefore are greatly involved in soil equilibrium processes. Sulfates of trace metals are also readily available to plants, and their occurrence in soils has practical importance in agriculture.⁶⁷³ Elemental sulfur application (at rate $300 \mu\text{mol/kg}$) decreases soil pH by 0.5 unit and increases the phytoavailability of several trace metals and thus, increases an effect of the bioremediation (Cimrin et al., 2007).

Chlorides as the most soluble salts that occur only in soils of arid or semiarid climatic zones. Chlorides' affinity for forming easily soluble complexes with Cd is of environmental concern (Wegglar et al., 2008). Increased levels of Cl (usually together with Na) restrict water availability to plants and reduce plant yield (Dang et al., 2006). The occurrence of natural organochlorines in sediments is an evidence for Cl interaction with organic matter in various environments (Müller, 1999).

IV ORGANIC MATTER

Natural organic matter (NOM) is nothing but broken down organic matter from flora and fauna. NOM in soil, soil organic matter (SOM) consists of a mixture of plant and animal products in various stages of decomposition and of substances that are synthesized chemically and biologically. This complex material, greatly simplified, can be divided into humic and nonhumic substances. Dissolved fraction of organic matter (DOM) is involved in several soil processes. NOM is widely distributed in soils, miscellaneous deposits, and natural waters. The amount of organic carbon in the earth as humus ($50 \times 10^{11} \text{ t}$) has been calculated to exceed that which occurs in living organisms ($7 \times 10^{11} \text{ t}$).²⁰¹

OM is accumulated in various environmental material (e.g., soil, peat, shales, petroleum, coal) as compared to average concentration in the Earth's crust (Weber¹⁸²). Meyer¹⁰⁹¹ concluded that the

biomass has also affected the Earth's surface chemistry, because the photosynthetic generation of free oxygen and carbon compounds contributes significantly to the diversity of redox potentials in both sedimentary and igneous-related processes of selection of metals at the source, during transport, and at the site of ore deposition. On the contrary, Rösler and Beuge¹¹³³ pointed out that the often discussed role of trace elements bound to organic substances is of much less importance in their behavior during the metamorphism than has been anticipated. Metamorphic processes of organic sediments involve the fractionation of trace elements with a general trend: (1) Hg, U, and I in peats, (2) Sr and F in lignite, (3) Pb, Cu, and Zn in hard coal, and (4) Mn and Cr in graphite.¹¹³³

Organic substances play a prominent role in biochemical weathering and thus in geochemical cycling of trace elements. Stevenson¹¹⁵⁷ discussed evidence both for and against their involvement in weathering processes. It seems more likely that humic acids (HA) and fulvic acids (FA) exhibit an activity of the same order as simple organic compounds in metal ion mobilization from soil minerals. The solubilization and transport of trace metals, mediated by humic substances, are cited by several authors.^{299,1157,1163} Tipping (1998) described the importance of HA and FA in binding of metal ions and proposed the mechanistic model (WHAM VI) for the prediction of metal partitioning in soil suspension.

The major portion of the OM in most soils results from biological decay of the biota residues. The end products of this degradation are humic substances, organic acids of low-molecular and high-molecular weights, carbohydrates, proteins, peptides, amino acids, lipids, waxes, polycyclic aromatic hydrocarbons, and lignin fragments. In addition, the excretion products of roots, composed of a wide variety of simple organic acids, are present in soils. It should be mentioned, however, that the composition and properties of the OM are dependent on climatic conditions, soil types, and agricultural practices. In soils contaminated with trace metals, and in particular with Cu, over the long term, there could be an expected increase in SOM content by reducing OM decomposition.^{390,1478} Similar effects have also been observed with other trace metals. This is of considerable importance in predicting the long-term environmental effects of the trace metal pollution.

The SOM controls several soil properties. These substances increase CEC of soils; from 20% to 70% of CEC value due to organic matter (e.g., Chernozems/Mollisols). Great sorption capacity for trace cations is beneficial in reducing activity of an excess of trace metals. On the contrary, organic by-products (municipal biosolids) may reduce bioavailability of some micronutrients. The adsorption of some metals (Cd, Ni, and Cu) is significantly enhanced at the presence of humic substances.¹⁰⁵⁷

The most stable compounds in soils are humic substances partitioned into the fractions of HA, FA, and humin, which are similar in structure, but differ in their reactions. Humic substances are of a coiled polymer chain structure and contain a relatively large number of functional groups (CO₂, OH, C=C, COOH, SH, CO₂H) having a great affinity for interacting with metal ions. Owing to a particular combination of different groups (mainly, OH and SH), humic substances are able to form complexes with certain cations. Some trace anions, such as B, I, and Se, are also well-known to be organically bound in soils. Humic substances are also easily adsorbed by clay and oxide particles in soil and water environments, and these responses are highly dependent on trace cations.^{779,799} Laxen¹⁰⁵⁷ emphasized a role of humic substances in the adsorption of Cd, Cu, Ni, and possibly Pb onto Fe hydroxides. It is evident that SOM highly control the adsorption/coprecipitation processes of most of the trace elements.

Estimated CEC values of humic substances vary from 200 to 500 meq/100 g, being higher for HAs and lower for FAs. General properties of humic substances are:

- Fulvic acids (fulvates)—have a low degree of polymerization, high acidity, and mobility; occur mainly in poor acid soils of a low biological activity.
- Humic acids (humates)—have spherocolloidal polymerization, medium acidity, and mobility; occur in weak acid and neutral soils of a high biological activity.

- Humins—are products of aging of humates and fulvates, have a high degree of polymerization and low acidity; occur in all soils.

Interactions between humic substances and metals have been described as ion exchange, surface sorption, chelation, coagulation, and peptization. It should be emphasized that the existence of a particular site for each cation is not easy to prove because the metal may be bound to two or more ligands from different molecules. All reactions between organic matter and cations lead to the formation of water-soluble and/or water-insoluble complexes. Organic matter and some decomposition products can act as reducing agents and assist in mobilizing some elements. Compounds acting as a reducing agent form complex ions with a number of cations, and also form a few sparingly soluble species. Trudgill¹¹⁶⁷ reported that humic matter in laboratory studies reduces a variety of metal ions such as: V^{5+} to V^{4+} , Hg^{2+} to Hg^0 , Fe^{3+} to Fe^{2+} , Cr^{6+} to Cr^{3+} , and U^{6+} to U^{4+} . The interaction of SOM with Cu, Pb, and Zn resulted in SOM changes: increased FA and decreased HA contents (Minkina et al., 2006).

Sholkovitz and Copland⁷²⁰ studied the complexing and chelation of trace elements with organic ligands in natural waters. Their studies led to the conclusion that solubilities of humic acid complexes with Fe, Cu, Ni, Cd, Cu, and Mn are the reverse of those predicted from inorganic solubility considerations. The complexing of these ions with humic substances led to the solubilization at high pH (range 3–9.5) and precipitation at low pH (range 1–3). Trace metals in natural waters are highly mobile due to their complexation, adsorption and reduction by humic material (Weber¹¹⁸²).

Organic matter is of importance in the transportation (and subsequent leaching) and accumulation of cations known to be present in soils and water as chelates of various stability and in supplying these ions to plant roots. The ion-exchange equilibrium has been extensively studied for determining the stability constant of metallo-organic matter complexes in soils. The values of stability constants determined by several authors described the ability of FA and HA to form complexes with metals (Table 4.5). Metal-fulvic acid complexes with lower stability constants usually are more readily soluble and thus more available to plant roots. The evaluation of several experiments,

TABLE 4.5
Stability Constants Expressed as Log K of Metal FA and HA Complexes at Various pH Levels of the Media

Cation	pH 3		pH 3.5	pH 5				pH 7
	FA (692)	HA (395)	FA (571)	FA (692)	FA (571)	HA (771)	HA (395)	HA (395)
Cu ²⁺	3.3	6.8	5.8	4.0	8.7	8.7	12.6	12.3
Ni ²⁺	3.2	5.4	3.5	4.2	4.1	—	7.6	9.6
Co ²⁺	2.8	—	2.2	4.1	3.7	—	—	—
Pb ²⁺	2.7	—	3.1	4.0	6.2	8.3	—	—
Zn ²⁺	2.3	5.1	1.7	3.6	2.3	—	7.2	10.3
Mn ²⁺	2.1	0	1.5	3.7	3.8	—	0	5.6
Cd ²⁺	—	5.3	—	—	—	6.3	5.5	8.9
Fe ²⁺	—	5.4	5.1	—	5.8	—	6.4	4.8
Ca ²⁺	2.7	0	2.0	3.4	2.9	—	0	6.5
Mg ²⁺	1.9	0	1.2	2.2	2.1	—	0	5.5
Fe ³⁺	6.1 ^a	11.4	—	—	—	—	8.5	6.6
Al ³⁺	3.7 ^b	—	—	—	—	—	—	—

References are given within parentheses.

^a Determined at pH 1.7.

^b Determined at pH 2.4.

however, elucidates that OM in soils has a relatively low influence on the uptake of trace metals by plants.¹³⁷⁵ It is still controversial and needs further examination, and perhaps study of the separated fraction of OM, with special emphasis on DOM compounds in soils.

The highest stability-constant values were reported by Takamatsu and Yoshida⁷⁷¹ for Cu^{2+} , Pb^{2+} , and Cd^{2+} complexed with HA at pH 5, and by Kitagishi and Yamane³⁹⁵ for Cu^{2+} , Zn^{2+} , Ni^{2+} , and Cd^{2+} at pH 7. Andrzejewski and Rosikiewicz²⁸ observed that Mn^{2+} , Co^{2+} , and Ni^{2+} complexes with HA were partly soluble, while those of Cu^{2+} , Fe^{2+} , and Cr^{3+} were insoluble. Augustyn and Urbaniak⁴⁰ also stated that higher retention by HA was of Fe^{2+} , Cu^{2+} , and Zn^{2+} as compared to other metallic ions. Fe^{3+} and Al^{3+} , however, form the most stable complexes with FA which greatly interfere with the crystallization of Al hydroxide polymorphs.⁴⁰⁶

The stability of metal complexes with FA and HA increases, in many cases, with increasing pH from 3 to 7 (Table 4.5). Findings presented by Gamble¹⁰⁰⁷ confirmed a significant effect of pH on the sorption of metals on HA (Table 4.6). This is best illustrated for Pb, as studied extensively by Hildebrand and Blume.³¹⁹ The binding of Fe^{2+} and Fe^{3+} by FA in solution below pH 5.0 is very strong and, apparently, cannot be exchanged easily by other metals. A relatively high value of the stability constants of Ca^{2+} suggests that this metal can compete with Zn^{2+} and Mn^{2+} in ion exchange processes. Most likely, however, several trace metals such as Hg, Fe, Cu, Cr, and Pb will readily form stable organic complexes with FA and, most probably, also with other organic compounds.

Analyses of fractionated organic acids from soils by Stepanova⁷⁵⁶ confirm the great affinity of FA for trace metals (Table 4.7). Mickievich et al.⁵³⁷ also reported a much higher concentration, mainly of Cu, Pb, and Ti in FA than was found in HA. Trace metals in soils tend to accumulate in the organic substances, and the lower the metal content, the higher the energy linkage of the metallo-organic groups.⁹⁰⁸

The commonly used value of the stability constant of a complex can be defined as an equilibrium constant of a reaction that forms a soluble complex or chelate. In order to include information about the behavior of insoluble complexes, the value of the stability index has been proposed by Cottenie et al.¹⁴⁸ This index describes the ratio of a given metal fixed with OM to its amount in inorganic fractions. The stability index for pure HA and FA shows that trace metals (Cu, Zn, Pb, Mn) form

TABLE 4.6
Effect of pH on Sorption of Metals on HA

Metal	Percentage of Initial Metal Concentration ^a		
	pH 2.4	pH 3.7	pH 5.8
Hg	99	98	98
Fe	81	96	100
Pb	19	80	96
Cu	12	59	97
Al	7	86	100
Ni	5	6	61
Cr	0	70	100
Cd	0	7	77
Zn	0	8	64
Co	0	2	45
Mn	0	3	13

Source: From Gamble, D. S., *The Importance of Chemical Speciation in Environmental Processes*, Dahlem Konferenzen, Springer-Verlag, Berlin, 217, 1986. With permission.

^a Initial metal content was 0.5×10^{-4} mol of each metal in 100 mL of solution.

TABLE 4.7
Trace Elements in SOM and in Clay Fraction (mg/kg)

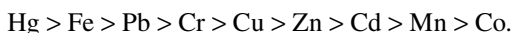
Surface Soil	Element	Content of Clay Fraction (<1 μm)			
		Total	Organic Matter	Humic Acid	Fulvic Acid
Chernozem	Cu	90	33.0	3.6	29.4
	Zn	116	41.5	3.4	38.1
	Mn	1110	262	Trace	254
	Mo	5	1.7	0.8	0.9
Podzol	Cu	44	17.9	1.2	16.7
	Zn	80	44.7	15.6	29.1
	Mn	1830	307	44	267
	Mo	3	0.7	0.2	0.5

Source: Adapted from Stepanova, M. D., *Microelements in Organic Matter of Soils*, Izd. Nauka, Novosibirsk, 105, 1976 (Ru).

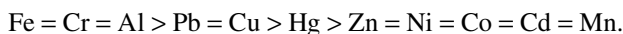
complexes several times more readily with HA than with FA, and that the highest proportion of Cu is fixed with HA over the range of pH 4–5, while with FA the range of pH is limited to 6–7. Both acids often show a higher affinity for Cu and Pb than for Fe and Mn. These findings agree with those reported by other authors (Van Dijk,⁸²⁰ Stevenson and Ardakani,⁷⁵⁷ Förstner and Müller,²⁴² Pauli,⁶⁰¹ Vlasov and Mikhaylova,⁸²⁵ and Schnitzer and Khan⁶⁹²) and indicate that the order of the stability constants of metallo-organic complexes, although quite variable depending on pH and other properties of the medium, can be presented in the following sequence:



Gamble¹⁰⁰⁷ emphasized, however, that because of a great number of variables in the natural system of soil organic polymers, the existence of an equilibrium function must be measured instead of an equilibrium constant. His data, obtained from the calculation based on weighted average equilibrium function theory, show the following order of metal affinity to sorption on HA, at pH 3.7:



Schnitzer and Kerndorff⁶⁹⁰ recently established the order of the affinity of metal ions to form water-insoluble complexes with FA. Although this order depends on the pH of the medium, it may be presented as follows:



Despite the diversity in these orders calculated for various experimental conditions, there is a general similarity in the estimation of two groups of metals, strongly and slightly fixed by organic polymers in soils.

The sorption capacity of HA increases with increasing acidity. Varshal et al.,¹⁵³⁰ determined amounts of sorbed metals by HA at pH 5–6, and gave the following values (in mg/kg of HA): Cd, 9; Au, 16; Sr, 17.5; Cu, 18; Y, 19; Os, 24; Yb, 28; Cs, 29.3; Ce, 31; and Pb, 120.

The solubility of FA–metal complexes is strongly controlled by the ratio of FA:metal; therefore, when this ratio is lower than 2, the formation of water-insoluble complexes is favored. There is a diversity, however, in the interpretation of metal ion binding by peat, because, as Bloom and McBride⁸⁰ reported, peat and HA are likely to bind, at an acid pH, most divalent cations (Mn, Fe,

Co, Ni, and Zn) as hydrated ions. The exception is the Cu^{2+} ion coordinating with functional oxygens of the peat which results in strongly immobilized Cu^{2+} binding. As Essington (vide Basta et al., 2005) described, soft acid metals (Cd, Hg) prefer soft base ligands (thiol) and hard acid metals (Fe, Mn) prefer hard base ligands (OH^- , COO^-), borderline acid metals (Cu, Zn, Pb) form complexes with a weak or strong base.

The index of OM affinities of trace elements in various coal samples was calculated by Gluskoter et al.²⁶⁹ These authors distinguished three groups of elements:

- With the highest organic affinity—Ge, Be, B, Br, and Sb
- With medium organic affinity—Co, Ni, Cu, Cr, and Se
- With the lowest affinity, but occurring in all organic fractions—Cd, Mn, Mo, Fe, Zn, and As

Histosols, soils formed from decomposed plant material, play a specific role in the distribution of trace elements in the biosphere. The elements which are easily taken up by plants and are likely to be fixed by OM of histosols appeared to be concentrated in peat soils. Lieth and Markert¹⁰⁶³ compared chemical composition of the peat bog with the nearby mineral soil, and emphasized the variable pattern of the element distribution. They concluded that Cd and Pb are more abundant in the peat than in the mineral soil, apparently due to aerial deposition. The affinity of humic substances to accumulate trace cations has great importance in their geochemistry. The so-called “geochemical enrichment” factors of HA that was extracted from peat can reach a value of 10,000 from very low concentrations of cations in natural waters.^{299,691} Trace elements migrating as anions (V and Mo) are reduced by HA and fixed in the cationic forms (VO^{2+} , MoO_4^{2+}). Metals complexed by FA presumably are more available to plant roots and soil biota than are those accumulated by HA which can form both water-soluble and water-insoluble complexes with metal ions and hydrous oxides.

Cottenie et al.¹⁴⁸ calculated that HA of a soil containing 4% humus may bind (in kg/ha): Pb, 4500; Fe, 17,929; Cu, 1517; Zn, 1015; and Mn, 913. The ability of HA to complex with metals was also calculated by Ovcharenko et al.⁵⁸⁷ and expressed, as follows (in g/kg of HA): Cu, 3.3; Zn, 3.3; Co, 3.2; Fe, 3.0, and Mn, 2.6. Sapek⁶⁸¹ showed that the ability of HA to fix cations differs widely, and that those isolated from the A_0 horizon of podzolic soil have about two times lower sorption capacity to metals than those extracted from the B_h horizon of the same soil.

In general, it can be expected that up to 50% of total trace element content is fixed by OM in mineral soils. These figures, however, can vary significantly.⁷⁵⁶ Based on the results of the incubation experiments on a wetland soil samples, Grybos et al. (2007) stated that in spite of bound forms of metals (to OM or/and to Fe-oxyhydroxides), their release is mainly by DOM. Thus OM is a main factor in controlling metal mobility in wetland soils.

Owing to the relatively insoluble complexes of HA with trace metals, especially in an acid medium, these complexes can be considered to be organic storage for trace metals in soils. The OM may act as an important regulator of the mobility of trace elements in soils; however, in the majority of mineral soils, organic matter does not exceed 2% of total soil weight; therefore, it cannot be of the greatest importance in overall controls of trace element behavior in soils. Organic matter fix and release ions and chemical compounds and thus act as reservoir of trace nutrients and contaminants. Chemical partition of chemicals into OM results in a “buffering” mobile TEs.¹⁰³⁰

A high OM content of soil has a complex influence on the behavior of trace elements. The deficiency symptoms of plants grown on drained peatland or moorland (histosols) may be the result of a strong retention of Cu, Zn, Mo, and Mn by the insoluble HA.¹³⁵ A strong fixation of Cu in soils rich in humus is the most common and may result in a high Mo-to-Cu ratio in forage that is toxic to cattle. Applying OM to soil, however, raises the number of microorganisms that can reduce several cations, mainly Fe and Mn, and, in consequence, increase their availability. Increased OM content in Pb-amended plots is due to an enhanced preservation of stable humus, perhaps because of newly formed Pb-organic complexes with HA and FA which are protected from microbial attack.⁹⁰³

However, there is also evidence that Pb complexes with low-molecular-weight humic substances were mobilized in the soil solution. On the contrary, some organic compounds present in root exudates and in humus can oxidize and therefore immobilize cupric compounds in soil.^{81,189} In general, the addition of OM increases the mobility (extractability) of Cu, Zn, Mn, and Fe in soil, but not their amounts bound to the residual fraction (Herencia et al., 2008).

Simple organic compounds, such as certain amino acids, hydroxy acids, and also phosphoric acids naturally occurring in soils, are effective as chelating agents for trace elements. Cation chelation is an important factor in soil formation processes, as well as in nutrient supply to plant roots. The solubility of metal complexes depends on both the binding strength and the mobility of the complex thus formed, which is determined mainly by the size of the organic group involved. Strong binding of metal to a low-molecular-weight organic substance will appreciably increase its mobility in soil (Figure 4.4). Organic acids of leaf litter are known to be active in the mobilization of trace metals in soils. An extract of pine needles dissolved more metals than an extract of oak leaves; in both cases, however, Cu and Zn were more readily complexed than were Co, Ni, and Cd.^{87,374} Despite a high mobilization of trace metals, forest soil litter is also well-known as an important sink of trace metal and radionuclide pollutants, as reported by Pavlotskaya,^{602,603} Van Hook et al.,⁸²³ and Schnitzer and Khan.⁶⁹² The ability of simple organic acids to solubilize trace metals may be of importance in their cycling. Rashid⁶⁴² calculated that each gram of amino acids occurring in the sediments may mobilize 4–440 mg of various metals, showing the highest affinity to Ni and Co and the lowest to Mn.

Several chelating agents are at present used in diagnostic extraction for available micronutrients in soils (Norvell,⁵⁷¹ Mengel and Kirkby,⁵³¹ and Lindsay⁴⁷⁷). Of those commonly used are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), which have been used for many years for determining plant-available trace elements in soils. Although the results differ when compared with other soil extractants and with uptake by plants, they are applied in many testing methods, and the ranges for critical levels are given for some micronutrients such as Cu, Zn, Mn, and Fe. The DTPA soil test has also been developed to assess pollution by trace metals of soils.¹⁴³ Soluble chelates of some trace metals, mainly Mn and Zn (i.e., Mn-EDTA; Na₂Zn-EDTA), are also effective as fertilizers. Pickering¹¹¹⁸ summarized data showing the ability of synthetic

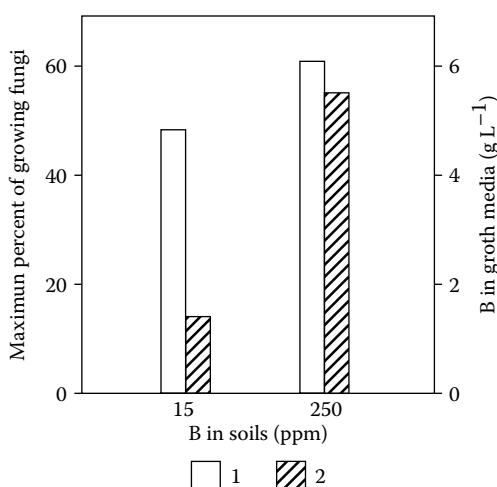


FIGURE 4.4 Tolerance of Actinomycetes from soils with various B contents to B concentrations in the growth media. (1) Growing fungi, in percent of total number; (2) maximum tolerable concentration of B in solution. (From Letunova, S. V., *Trace Element Metabolism in Animals*, Churchill Livingston, Edinburgh, 549, 1970. With permission.)

chelating agents (EDTA and Na-citrate) to displace metal ions from soil components. Both agents easily mobilized metals (Zn, Cd, Cu, and Pb) fixed by kaolinite, illite, and montmorillonite. The mobilizing effect was moderate or very small when those metals were retained to the following substrates: $\text{Fe}(\text{OH})_3$ gel, MnOOH , CaCO_3 , and humic acid.

Recently, attention has been focused on the occurrence and function of proteins in terrestrial ecosystems (Quiquampoix and Burns, 2007). These compounds exhibit a strong affinity for solid–liquid interface processes in soil. Especially, the presence and fate of prions (specific proteins of infectious properties) are a subject of recent studies (Johnson et al., 2006; Rigou et al., 2006; Rao et al., 2007). These originate mainly from animal urine, easily bind to soil particles (mainly to montmorillonite and SOM) and persist in soil for years.

V ORGANISMS IN SOILS

Living organisms, often referred to as the soil biota, composed of fauna and flora of various dimensions (macro-, mezo-, and microbiota), occur abundantly in soils. At the microbiota level, the boundary between plant and animal cells becomes blurred. The importance of living organisms as reflected in the biological activity of soils has been discussed in many textbooks.^{187,651,856,898} Several species of biota are known to be useful indicators of soil pollution by trace elements. However, growth, reproduction, and metabolic activities of biota also are sensitive to other soil variables. The Eh–pH system and organic matter content are especially important. Humic substances are known to have both beneficial and deleterious effects on biota caused by binding or mobilization of metals. It was observed that increased trace element levels have an adverse effect on the natural regulation of the soil biota.⁹⁸²

A MICROORGANISMS

The abundance of microorganisms in topsoils varies with soil and climatic conditions and may reach as much as 20% of the total biota of a soil system. There is no easy way of knowing with certainty the biomass of microorganisms because this quantity can be determined only indirectly. The maximum weight of soil biota given by Richards⁶⁵¹ for a hypothetical grassland soil corresponds to 7 t/ha of microbiota (bacteria and fungi) and to 1.3 t/ha of mezobiota. Kovalskiy et al.⁴²² calculated that the biomass of bacteria and fungi present in the plow zone of soil (20 cm depth) ranges from 0.4 to 1.1 t/ha. The biomass of bacteria varies significantly during the growing season, and may increase about three times from spring to fall.⁴²¹ Keller (1997) identified in soil solution microscopic cells, *protists* (a diverse group of eukaryotic microorganisms, probably of the kingdom *Protoctista*) and suggest that they might be an indicator of soil pollution.

Microorganisms are very important ecologically because they are the producing, consuming, and transporting members of the soil ecosystem and therefore are involved in the flow of energy and in the cycling of chemical elements. Thus, the microbiota is responsible for many different processes, from mobilization to accumulation of chemical elements in soils. Although microorganisms are sensitive to both deficiencies and excesses of trace elements, they can adapt to high concentrations of these elements in their environment. Microbe–clay mineral interactions are responsible for the biological reduction of Fe^{3+} which have great affinity for the surface-complexation sites and thus increase the immobilization of trace cations in natural environments (Jaisi et al., 2008).

The role of microorganisms in geochemical cycling of the major elements is relatively well-understood on the global level. The biogeochemical cycling of trace elements has received much less attention. With the recognition that microbial transformations of compounds of these elements can result in some problems of soil fertility as well as in the formation of some environmental pollution or detoxication processes, the importance of microbiota in cycling of trace elements, especially trace metals, has been more extensively studied. Processes of microbial methylation can occur in oxic and anoxic soil conditions, and can highly influence the behavior of some trace elements.

Several elements, such as As, Hg, Se, Te, Tl, Pb, and In, are known to be biologically methylated in soils.¹²⁰¹ However, abiotic processes of methylation can also occur in soil.

The basic microbial phenomena in cycling processes in the soil environment are:

- Transport of an element into or out of a cell
- Charge alteration of an element
- Interaction of an element with organic compounds to become a functional part of the system
- Complexing an element by organic acids and other compounds produced by microorganisms
- Microbial accumulation or mobilization of an element
- Microbial detoxication of contaminated soil at a site
- Microbial methylation of an element

The most important microbial function in soil, however, is the degradation of plant and animal residues. It has become apparent that the quantity of trace elements needed or harmful for the growth of microorganisms also influences the biological activity of soils.

All available evidence indicates that low concentration of trace elements stimulate bacterial growth in soil, but a higher content is harmful, being usually most toxic to the bacteria that fix free N and to nitrifying bacteria.^{505,812} Of the 19 trace elements studied by Liang and Tabatabai,⁴⁷¹ all inhibited mineral N production in soils. At the concentrations of 5 $\mu\text{M/g}$ of soil, the most toxic elements were Ag^+ and Hg^+ , while the least toxic were Co^{2+} , As^{3+} , Se^{4+} , and W^{6+} . Trace metals especially are known for their toxicity to microbiota, with fungi and actinomycetes having the most resistance. Reduction of microbial growth and enzymatic activity is often reported for soils contaminated by trace metals.^{88,733,814} Elevated metal concentrations are responsible for commonly observed decreases in symbiotic and nonsymbiotic N_2 -fixation.¹⁰⁸⁹ Doelman⁹⁸² summarized reported effects of different concentrations of trace metals on microbial activities in soils. The data presented indicate that Cd, Hg, Ni, and Zn are toxic at lower levels than the other metals (Table 4.8). Atmospherically borne metals, most often associated with H_2SO_4 and HNO_3 , cause significant damage to soil organisms. These effects are related either to direct toxic impact of trace metals and to lowering of pH, or to general deterioration of the habitat quality. Bengtsson and Torstensson⁹³⁹ reviewed several studies on the inhibition of soil respiration and of turnover of carbon and nutrients in metal-polluted soils. Mathur et al.⁵¹⁵ showed that the effect of a naturally high Cu content of histosols is most suppressive on levels of accumulated enzyme activities involved in the degradation of the major components of organic debris in soils. A low rate of decomposition of vegetation having a high concentration of Pb and Zn is apparently due to the same processes in nature.⁸⁷⁷

Suppression and/or stimulation of biosynthesis of microorganisms by trace metals depend on the nature of the organisms, the kind of metal, and the pH of soils. Even within one species, the range of required or inhibitory concentrations of a given metal varies significantly.⁴²¹

On the basis of data presented in the monograph by Weinberg,⁸⁵⁶ it may be generalized that the highest concentration of Fe, Mn, and Zn required by various microorganisms (fungi, bacteria, bacilla, and actinomycetes) was around 100 $\mu\text{M/L}$. The inhibitory concentrations of these elements on vegetative growth and secondary metabolism of microorganisms have also been established at the above range.

Microorganisms take up trace elements, several of which play important metabolic functions.^{344,614,467} It has been shown by Kokke,⁴⁰⁷ however, that cells of microorganisms may show quite variable affinities for radionuclides that are necessarily related to their biological function (Table 4.9).

Cumulative pools of trace elements in the mass of microbiota have been calculated as follows (in g/ha): Ni, 350; Cu, 310; Zn, 250; Co, 150; Mo, 148; and Pb, 8.4, which corresponds to 0.002–0.21% of their total abundance in the 20-cm topsoil level (Kovalsky et al.⁴²²). Microbioaccumulation of trace elements may be of great importance both in the cycling of elements in soil and in their

TABLE 4.8
Toxic Effects of Trace Metals on Microbial Activities in Soils

Metal Concentration in Soils (mg/kg)	Inhibited Process	Reported	
		Sometimes	Always
<10	Soil respiration	Cd, Hg, Ni, Zn	
	N-mineralization	Hg	
	Nitrification	Hg	
<100	Soil respiration	Cd, Cu, Pb	Hg
	N-mineralization	Cd, Cu, Ni, Pb	Hg
	Nitrification	Cd, Cu, Ni, Zn	Hg
<1000	Soil respiration		Cd, Cr, Cu, Ni, Zn
	N-mineralization		Cr, ^a Cu, Ni, Zn
	Nitrification		Cd, Cr, ^a Cu, Ni
<10,000	Soil respiration		Pb
	N-mineralization		Cd, ^b Pb
	Nitrification		Pb, Zn

Source: From Doelman, P., *Microbial Communities in Soil*, Elsevier Appl. Sci. Publ., London, 369, 1986. With permission.

^a Concentration given for about 500 mg/kg.

^b Concentration given for about 3000 mg/kg.

phytoavailability. Microorganisms are known to have an impact on solid–liquid interface processes that control sorption by both minerals and organic matter. Perelomov and Yoshida (2008) reported that microorganisms affected on lanthanides sorption by quartz and goethite. The impact, however, was significantly controlled by soil pH.

Increased levels of trace elements can disturb soil microbial processes. On the contrary, bacterial impact on trace metal behavior may be significant, especially in soil amended with sewage sludge, where bacterial leaching of metals have a practical application (Olson¹¹⁰⁶). Apparently, soil

TABLE 4.9
Radionuclide Uptake by the Yeast *Candida humicola* as a Function of Time

Radionuclide	Initial Concentration in Growth Media (μM/L)	Time of Growth (days)				
		1	2	4	8	16
		% of Initial Concentration				
⁸⁹ Ce	40	93	95	98	99	99
⁵⁵ Fe	40	68	83	95	95	95
⁶⁵ Zn	64	60	60	60	75	99
⁸⁹ Sr	40	18	18	18	37	99
¹³¹ I	20	16	18	25	—	25
¹⁰⁶ Ru	40	15	30	45	60	75
⁶⁰ Co	40	3	5	5	18	77
⁶³ Nd	40	3	3	3	5	12
¹³⁷ Cs	40	1	2	2	3	5

Source: From Kokke, R., *Radiotracer Studies of Chemical Residues in Food and Agriculture*, IAEA, Vienna, 15, 1972. With permission.

microorganisms are more sensitive than other terrestrial organisms to increased levels of metals, thus the assessment of their toxicity has recently become the subject of investigations (Brooks et al., 2005; Bhattacharya et al., 2008). These authors reported that the N fixation in clover is the most sensitive to an excess of Cd and Zn. However, the adverse concentration effects on the potential nitrification rate differ greatly between soils and varied for Cd from 7 to 55 mg/kg and for Zn from 107 to 1764 mg/kg. Increased levels of F (up to 189 mg/kg) has been reported to decrease microbial activity by 5–20% of those in the uncontaminated soil (Tschenko and Kandeler, 1997). In soil systems, Hg, Cd, and As seemed to be the most harmful to ammonification processes, while Cu greatly reduced phosphate mineralization rates.^{762,813}

The microbial activity is highly governed by soil properties. As microorganisms are involved in SOM transformations, their activities are associated with OM content. Czaban and Wróblewska (2005) observed that microbial transformation of Cd species from the solid phase to species soluble in DTPA was lower in fine-texture soil with low SOM content (1.1% C) than in sandy soil with higher SOM content (4.2% C). Smolders et al. (2004) suggested that the most significant factor controlling different reactions of microbial processes to increased Zn concentrations is the variable community tolerance. Community level of physiological profiles of soil microorganisms have not changed under different levels of Cd, Zn, and Pb that indicate their developed tolerance to increased contents of metals (Niklińska et al., 2004). Microbial community-level adaptations through the development of resistance mechanisms to the types and local levels of metals also were observed in polluted lake sediments (Hoostal et al., 2008). The adaptation of microorganisms to high concentrations of trace elements has been well-illustrated by Aristovskaya³⁵ and Letunova⁴⁶⁴ for several elements such as Fe, Mn, Mo, Se, and B (Figure 4.5). The adaptation is also well-shown in various microbiogeochemical processes described in detail by Babich and Stotzky,⁴¹ Gadd and Griffiths,²⁵¹ Zajic,⁸⁹⁸ and Chien et al. (2008). Strains of streptomycetes isolated from U mining site exhibit a tolerance to increased concentrations of several trace metals (Schmidt et al., 2007). The sensitivity of microorganisms (mainly fungi) to different concentrations of trace elements has often been used in the determination of the availability of micronutrients such as Fe, Cu, Zn, and Mo.^{531,572}

Since trace metals are toxic to microorganisms even at relatively low concentrations, they have evolved efficient mechanisms to detoxify the metals. Chakrabarty⁹⁶¹ and Silver¹¹⁵⁰ described a variety of reactions that reduce the toxicity associated with entry of the metal inside the cell. Most common reactions depend on processes of oxidation, reduction, and alkylation.¹¹⁰⁶ Other reactions of the bacterial resistance to metals are energy-dependent processes of the efflux of the metal from the cell, and precipitation of the metal at cell surfaces. Metal–microbe interactions evolved resistance mainly against such metals as Ag, Cd, Cr, Cu, Fe, Hg, Pb, Ni, and Zn. The resistance of microorganisms to other trace elements was also observed, but the mechanisms involved are not yet understood.¹¹⁵⁰

Somers⁷⁴⁶ reported that the fungicidal action of trace cations is due primarily to the formation of an un-ionized complex with surface groups (e.g., phosphate, carboxyl, and sulfhydryl). This author showed that there is a relationship between the toxic concentration of the metal ion and its electronegativity value. The order of toxicity of aqueous solutions of nitrates and sulfates against conidia of *Alternaria tenuis* was given by Somers⁷⁴⁶ as follows:



Processes of alkylation and dealkylation control the toxicity and behavioral properties of some trace elements to a great extent. Microbial methylation under environmental conditions was observed for As, Hg, Se, Sn, and Te. On a chemical basis, however, one would expect Au, Bi, Pb, Pd, Pt, Sb, and Tl to have a potential capability for forming methylated compounds.⁹³⁵ Indeed, some forms of Pb and other metals are known to undergo methylation under soil conditions. Beijer and Jernelöv⁹³⁵ stated that whether the methylation is a biological or a purely chemical reaction is still under debate, and that it is still unclear if organic Pb²¹ may be methylated. Also Craig and Rapsomanikis⁹⁷⁰ focused

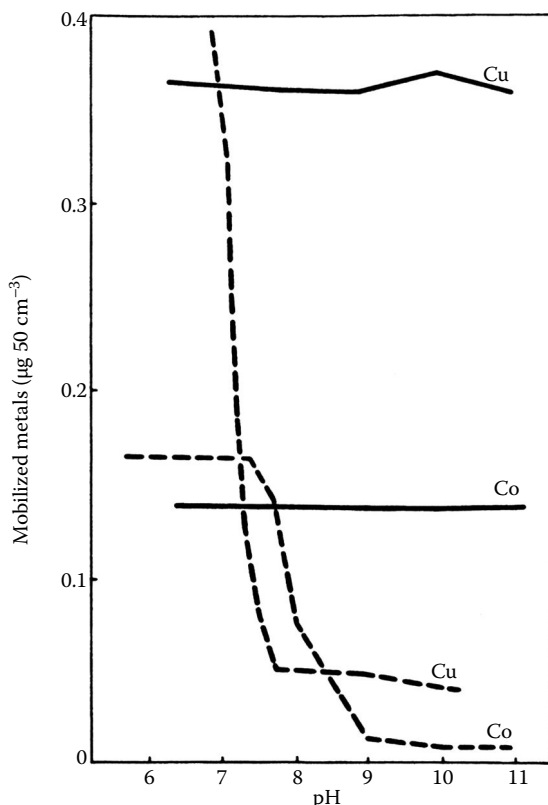


FIGURE 4.5 The effect of pH on the solubility of Co and Cu mobilized by aerobically decomposing alfalfa. Solid lines, complexed metals, broken lines, control solution of CuCl_2 , or CoCl_2 alone. (From Bloomfield, C., *The Chemistry of Soil Processes*, John Wiley & Sons, New York, 463, 1981. With permission.)

attention on the identification of chemical methylating agents known to be present in the environment which are suitable substances for the methylation of metals. Recent studies of Chau et al.⁹⁶⁵ indicated that transmethylation reactions between organometals and metal ions occur in aqueous solutions in both biotic and abiotic systems. Results of these studies suggest that, for example, alkyl-lead or methyltin compounds could be potential methylating agents for the formation of other methylmetals. Thus, alkylation processes in soils are not solely of a bacteriological origin.

The physicochemical relationship between bacteria and mineral surfaces leads to diverse effects of dissolution and secondary precipitation of trace metal ions, including changes in their valence and/or conversion into organometallic compounds. There is a large number of biologically induced minerals (BIM) especially of Fe and Mn. The major metabolic processes that cause deposition and/or dissolution of Fe and Mn minerals are oxidation and reduction of metals, metal sulfate oxidation, and metal sulfide reduction (Frankel and Bazylinski, 2003). These processes are the most important factors governing the solubility, and thus, the bioavailability, of these metals in soils. Many bacterial species are implicated in the transformation of trace element compounds, including even neoformation of certain Fe and Mn minerals.¹⁴⁰ Bacteria also play the most important role in the formation of metal concretions, which affects the mobility of metals in soils.⁸¹ The mobilization of metals on a large scale is of geochemical significance since it may lead to the ore formation (e.g., Cu, U). Such processes are the results of the growth of acidiphilic and/or chemolithotrophic bacteria that derive their energy from the oxidation of reduced (or partially reduced) sulfur compounds and metal salts.⁹⁶¹

A complex balance of trace elements required for the microbial activity is of importance in soil productivity. The quantities of specific trace elements available to soil microorganisms can be the critical determinant in the establishment of a disease condition of certain plants. The trace element competition between plants and microorganisms is apparent in various reports, and it may react in different ways. Microbially induced decreases in the availability of trace elements result from a considerably high accumulation of certain elements by microbiota and also from the biological oxidation of compounds of these elements. On the contrary, microbiological increases of availability, are caused by microorganisms capable of reducing certain compounds (principally, Mn and Fe) and also by their variable bioaccumulation of trace elements (Table 4.10). Highly elevated levels of trace elements, particularly of As, Cd, Cu, Cr, Hg, Pb, and Sb, are known to reduce the growth and decomposing capacity of soil microbes.⁹⁶³ Effects of these processes are observed in reduced capability to decompose organic pollutants (e.g., pesticides, oil) and organic debris in soils. Negative impact of these metals on the decomposition of organic matter, on the mineralization of N and P compounds, and on the activity of N fixation is commonly reported (Table 4.8). However, it is not easy to predict microbial consequences of soil pollution with metals because of variable reduction in the activity of one species, with increasing tolerance in other species.¹¹⁵⁰

Soil fumigation or steaming and many fungicides kill the fungi and therefore may interfere with the ability of plants to absorb micronutrients. The mechanisms of these phenomena are not yet fully understood, however, they may be related to an imbalance of soil microorganisms and their participation in the transport of ions into or within biological systems. As Martin^{510a} reported, variable effects in plants of B, Cu, Li, Mn, and Zn toxicities or deficiencies of Cu, Mn, and Zn were found following soil fumigation.

Gadd and Griffiths²⁵¹ concluded that two main types of metal uptake by microorganisms can occur; the first involves nonspecific binding of the cation to cell surfaces, slime layers, extracellular matrices, and so on, while the second involves metabolic-dependent intracellular uptake. The polygalacturonic acid, a common constituent of the outer slime layer of bacterial cells, can complex several trace metals. Chintalapati et al. (2008) isolated from aquatic bacterium (*Aquifex aeolicus*) enzymes (ATPases) that are involved in the trace metal ion transport through the membrane.

The adsorption of trace elements by microorganisms differs widely, as is shown in Tables 4.9 through 4.11. Although the mass of microbiota in soils has been calculated to be in the range of

TABLE 4.10
Bioaccumulation of Cu, Mo, and V by Microbiomass in Topsoils at Various Seasons

	Cu		Mo		V	
	Soil (mg/kg)	Biomass (kg/ha)	Soil (mg/kg)	Biomass (kg/ha)	Soil (mg/kg)	Biomass (kg/ha)
Low content of elements	48	0.004 (Sp)	6	0.0013 (Sp)	66	0.002 (Sp)
		0.006 (Sm)		0.002 (Sm)		0.003 (Sm)
		0.028 (Fl)		0.009 (Fl)		0.013 (Fl)
High content of elements	270	0.60 (Sp)	72	0.075 (Sp)	840	0.124 (Sp)
		0.25 (Sm)		0.031 (Sm)		0.052 (Sm)
		0.22 (Fl)		0.029 (Fl)		0.049 (Fl)
Control soil (chernozem)	73	0.019 (Sp)	10	0.005 (Sp)	148	0.005 (Sp)
		0.069 (Sm)		0.017 (Sm)		0.019 (Sm)
		0.059 (Fl)		0.013 (Fl)		0.015 (Fl)

Source: Adapted from Kovalskiy, V. V. and Letunova, S. V., *Tr. Biogeochem. Lab.*, 13, 3, 1974 (Ru).

Note: Sp, spring; Sm, summer; Fl, fall.

0.X–X t/ha, the greatest amount of metals fixed by microorganisms are the following (in g/ha): Ni, 350; Cu, 310; Zn, 250; Co, 150; Mo, 148; and Pb, 8.4, which corresponds to 0.002–0.216% of their total abundance in the 20 cm topsoil level of 1 ha.^{422,465} More than 80% of microorganisms are believed to be adsorbed to soil organic matter and clay minerals.⁸⁸⁴ Therefore, comparisons of results obtained for pure cultures of microorganisms may differ from those naturally occurring in soils.

Calculations made by Kovalskiy et al.⁴²² and Letunova and Gribovskaya⁴⁶⁵ indicated that at the annual rate, the total biocycling of about 11 generations of microbiota may, on the average, involve the following amounts of trace metals (in kg/ha): Ni, 147; Zn, 104; Cu, 78; and Co, 28. Trace elements fixed by microbiomass may be much higher than these values for soils that increase their levels, as has been shown by Krasinskaya and Letunova.⁴²⁶ Microbioaccumulation of trace elements may be of great importance both in the cycling of trace elements in soil and in their availability to plants. Fungi and actinomycetes are the most resistant microorganisms to high concentrations of trace metals, while nitrifying and rhizosphere microorganisms are the most sensitive.

Various waste waters, as well as slurries used for soil irrigation and amendment, can be sources of microbial and other pathogenic organisms of a serious health hazard to humans and animals. This problem has been reviewed by Kristensen and Bonde.⁴²⁹ Bacterial leaching of trace metals from sewage sludges is, however, a practical application of the biotransformation of the forms of chemical elements.^{694,1106} Bioleaching of trace metals from contaminated soils has been applied recently. The benefit effect of bacteria involved in S oxidation–reduction in the solubilization of some metals (Cd, Cr, Cu, Pb) is due to decreasing soil pH (Nareshkumar et al., 2008).

The rhizosphere flora plays a special role in the bioactivity of soils and the availability of nutrients. Although effects of mycorrhizal fungi have been almost always ascribed to an increased phosphate uptake, some observations indicate that they may also influence micronutrient supply (Turnau et al., 2005). Studies conducted by Turnau et al. (2001) revealed variable distribution of macro- and microelements among various tissues of mycorrhizas. As Lambert et al.,⁴⁵⁶ Woldendorp,⁸⁸⁴ and Turnau¹⁵²⁴ reported, Zn, Cu, and Sr are the chief elements supplied to plants by a given type of

TABLE 4.11
Trace Elements in the Biomass of *Bacillus megaterium* growing in Different Media (mg/kg)

Element	Growth Medium ^a	
	Soil Rich in Cu, Mo, V	Soil Poor in Cu, Mo, V
Ag	<0.14–3.6	<0.14–0.51
Ba	46–368	<24–112
Be	<0.3–4.2	<0.3–2.1
Co	<0.3–14	<0.6–8
Cr	0.8–27	<0.5–17
Cu	10–98	4.5–39
Mo	3.4–21	1.2–6.2
Ni	<0.2–16	<0.7–12
Pb	<1.3–38	<0.8–8.7
Sr	2.3–55	1.7–7
V	4.3–28	3.2–15

Source: Adapted from Letunova, S. V. and Kovalskiy, V. V., *Geochemical Ecology of Microorganisms*, Izdat, Nauka, Moscow, 146, 1978, (Ru).

^a Growth medium was agar-agar with added soil extracts.

mycorrhiza. Organic acids (citric, tartaric, fumaric, and glutaric) associated with the rhizosphere may contribute to mobility/transport of several trace elements (Schwab et al., 2008). Some negative effects occurring in rhizospheres may be observed when anaerobiosis around the root surface due to a high oxygen demand of microflora leads to the formation of ferrous iron compounds which are taken up by plants to concentrations that cause the physiological disorder known as Fe toxicity.⁸⁰⁷ The presence of mycorrhizal symbiosis has also been demonstrated in plants, especially hyperaccumulating plants which are being used in the phytoextraction of metals (Skinner et al., 2005). Arbuscular mycorrhizal fungi (AMF) exhibit various mechanisms in controlling metal uptake by plants (Biró et al., 2006). Lebeau et al. (2008) reported that some rhizobacteria and AMF might be involved in the bioaugmentation for the bioremediation of multicontaminated soils. AMF and phosphate amendments prevent trace-metal bioaccumulation and their transfer from roots to shoots in tropical grass species (Soares and Siqueira, 2008).

Both bacteria and fungi growing under low Fe stress produce small molecular weight organic compounds, siderophores, of variable composition, mainly mixed-type catecholate and hydroxamate. The role of these compounds is to accumulate Fe in an easily available form to microorganisms. Siderophores may complex with trace metals, especially with As, Cd, Ni, Pb, Sn, Co, and Cu, and are proposed for As decontamination of soil (Nair et al., 2007). Soil bioaugmentation with *Pseudomonads*, as siderophore producers, is proposed to increase the bioavailability of metals for phytoextraction purposes (Braud et al., 2007).

B INVERTEBRATES

Any species of soil fauna (mezo- and macrobiota) participating in the trophic chain may reflect chemical composition of the soil. Lumbricid earthworms seem to be of greatest importance as indicator species in the terrestrial ecosystems. Earthworms may constitute up to 80% of the total biomass of the soil fauna, and because of their relatively large biomass, provide a significant food source for many species of several predators (e.g., birds, small mammals). Ma¹⁰⁷⁹ showed that the accumulation of trace metals in mole tissues reflects the bioavailability of these metals to earthworms. Metals accumulated in both small mammals and earthworms do not consistently reflect the metal contents of soils (Table 4.12). In most cases, however, their accumulation in earthworms can be relatively well-predicted (Table 4.13). Ma¹⁰⁷⁸ emphasized that in the ecosystems where earthworms comprise a large proportion of the soil fauna biomass, the bioaccumulation of metals, as high as up to 3500 mg/kg Zn, can be potentially hazardous to predatory animals. These findings indicate that only Cd and Zn are significantly enriched in the worms. However, under specific soil conditions, as for example high acidity, low Ca content, or low CEC value, other trace metals can also be easily taken up by earthworms. Based on laboratory and field observations, Ma¹⁰⁷⁷ gave the following order of increasing concentration factors of metals in worms in various soils:

$$\text{Cr} < \text{Mn} < \text{Fe} < \text{Ni} < \text{Pb} < \text{Zn} < \text{Cd}.$$

Ma et al.¹⁰⁸⁰ reported that *Lumbricus rubellus* easily accumulated Cd, Zn, and Pb from acid soils. Saxe et al. (2001) concluded that metal concentrations are mainly due to dermal exposure. Becquer et al. (2005), on the contrary, indicate that the ingestion of metals bound to soil particles is likely to be a more important uptake route than the dermal uptake of dissolved forms of metals. Lowe and Butt (2007) presented a critical review of earthworm use in ecotoxicological studies, mainly due to difficulties with experimental design and interpretation of results.

Soil parameters, and especially soil pH, control metal availability to earthworms, to variable extent (Conder et al., 2001). Thus, the demonstrated influence of soil factors on element concentrations in earthworms is related to the effect of soil properties on metal availability to organisms in the terrestrial ecosystems. Reduced abundance of earthworms in soil under the long-term sewage

TABLE 4.12
Metals in Surface Soils and Earthworms (mg/kg)

Metal	Soil	Earthworms	Ratio, Worms/Soil	Reference
Cd	2	15	7.5	339
	4	4	1	339
	1.6	11.1	6.9	264
	0.9	14.4	16	264
	1.1	18	16	160
	0.6	12	20	160
	0.1	2.7	27	160
	4.1	10.3 ^a	27.6	179
Cu	0.16	6 ^b	37.2	1104 ^a
	20	13	0.65	339
	252	11	0.04	339
	335	11	0.03	339
	52	28	0.53	160
	26	18	0.69	160
	9	5	0.55	160
	11	8.5 ^b	0.78	1104 ^a
Hg	3.8	1.29 ^c	0.33	111
	0.1	0.04 ^c	0.40	111
	0.32	0.31 ^b	0.97	1104 ^a
Mn	1330	82	0.06	339
	226	28	0.12	339
	164	27	0.16	339
	214	63 ^b	0.04	1104 ^a
Ni	26	31	1.19	264
	18	29	1.61	264
	12	32	2.66	264
Pb	1314	3592	2.73	339
	629	9	0.01	339
	700	331	0.47	264
	94	101	1.04	264
	170	62	0.36	160
	20	9	0.45	160
	870	109 ^a	0.12	160
Zn	138	739	5.35	339
	992	676	0.68	339
	219	670	3.05	264
	49	400	8.16	264
	275	2000	7.27	160
	40	900	22.50	160
	81	662 ^a	8.17	179
	76	256 ^b	3.4	1104 ^a

Note: Element concentrations expressed on dry weight basis. Organisms analyzed are *Lumbricus rubellus* or *Lumbricus terrestris*, except as indicated.

^a Other Invertebrata.

^b *Denolrobaena octahedra*.

^c FW basis.

TABLE 4.13
Effects of Increasing Concentrations of Metals in Soils on Their
Accumulation in Earthworms (mg/kg)

Metal	Soil	Lumbricus Species	Concentration Factor ^a
Cd	0.1	19 (8) ^b	190
	6.0	79 (69)	13
	9.2	114 (57)	12
Cu	7	20 (17)	2.8
	25	28 (21)	1.1
	40	28 (23)	0.7
Pb	24	12 (41)	0.5
	115	25 (41)	0.2
	135	25 (20)	0.1
Zn	35	730 (837)	20
	737	1474 (1525)	2
	1015	1789 (1164)	1.7

Source: From Ma, W., *Bull. Environ. Contam. Toxicol.*, 39, 933, 1987. With permission.

^a Ratio worms to soil.

^b Values predicted by Ma are in parentheses.¹⁰⁷⁹

sludge application indicates detrimental impact of elevated concentrations of metals: Cu, Ni, Zn (Creamer et al., 2008).

Roth-Holzappel^{1130a} analyzed species of invertebrates of the spruce forest ecosystem in Central Europe. She found that mainly essential elements (e.g., Cu and Zn) were accumulated in primary consumer groups. A concentration of other trace elements with increasing trophic levels was not confirmed, with the exception of Ni and Cd, which are highly mobile in environmental compartments. Increased availability of some metals (Cd, Cu, and Zn) to snails in the presence of earthworms suggests interaction mechanisms between biota species and nonbiota compartments (Coeurdassier et al., 2007).

Several authors discussed the use of earthworms as indicators for the bioavailability of trace elements (Edwards et al.,¹²⁸⁸; Conder et al., 2001; Saxe et al., 2001; Spiegel, 2002). Yoshida et al. (2005) studied the uptake of 33 elements by earthworms (*Eisenia foetida*) and reported lower transfer factors (TF) for Al, Sc, Ti, Y, Nb, and lanthanides than for all other elements. They concluded that earthworms may be candidate indicator organisms for environmental radiation studies. However, many factors hampered quantitative determination of the degree of soil metal availability to these biota. Trace metals, and especially Cu, are likely to concentrate in chloro-genous tissue (pigment) of earthworms (Carpene et al., 2006). In soils highly contaminated by trace elements, mezo- and macrobiota are decreased, their metabolism is inhibited, and finally all organisms may vanish. Spurgeon et al. (2008) reported that among trace metals, the most widespread risk to soil fauna was observed for Zn and Cd.

5 Trace Elements in Plants

I INTRODUCTION

The trace element (TEs) metabolism of plants has been extensively studied and the basic information on many topics is available in monographs on plant physiology or plant nutrition. The metabolic fate and role of each TE in plants can be characterized in relation to some basic processes such as:

- Uptake (absorption), and transport within a plant
- Enzymatic processes
- Concentrations and forms of occurrence
- Deficiency and toxicity
- Ion competition and interaction

TE concentrations in plants are highly associated with the chemical composition of growth media. Plant responses to TEs in soils depend on several factors, however some general trends, expressed by plant/soil Transfer Factor (TF) can be presented as generalized values:

- 10: Cd
- 1: B, Br, Cs, Rb
- 10^{-1} : Ag, Co, Cu, Ge, Hg, Mo, Pb, Sr, Te, Zn
- 10^{-2} : Be, As, Li, F, I, Mn, Ni, Sb
- 10^{-3} : Ba, Bi, Ga, Fe, Se, V, Tl, Zr

The reaction of plants to chemical stresses that are caused by both deficiencies and excesses of TE cannot be defined exactly because plants have developed during their evolution and course of life (ontogeny and phylogeny) several biochemical mechanisms that have resulted in adaptation to and tolerance of new or chemically imbalanced environments. Therefore, this always should be investigated for a particular soil–plant system. Plants reveal various tendencies in the uptake of TEs. Three general uptake characteristics can be distinguished: accumulation, indication, and exclusion. To a large extent, this depends on the specific ability of plants and huge differences in metal uptake between plant species. Also, between genotypes of a species, great variability has been demonstrated in many studies. Alexander et al. (2006) described general genotypic variations comparing tendency to the TE accumulation by vegetables: (1) legumes—low, (2) root vegetables—moderate, and (3) leafy vegetables—high. Also Peris et al. (2007) reported that significantly higher TE content (with an exception of Zn) was in lettuce than in artichoke.

Mechanisms of plant adaptation to the TE excess in growth media may be related to several processes, such as:

- Complexing and chelating of ions outside plant cells (mainly roots)
- Binding of ions to cell walls
- Selective uptake of ions
- Immobilization in various organs as immobile compounds, including minerals
- Restructured influx through the plasma membrane
- Release by leaching from foliage

- Extraction from leaf tips in forms of salts
- Volatilization of toxic compounds
- Efflux of element excess from roots
- Removal of elements with falling leaves/needles

A number of various plants are known as medicinal herbs and have been used for a very long time (possibly since Neanderthal man) to cure illness. Although a curative agent is mainly associated with organic compounds such as glycosides or alkaloids, TEs can have additional impact. Most medicinal plants belong to a kind of weed that can accumulate a greater amount of TEs than other plants. A good example is dandelion, often used in herb medicine and also as a nutritional plant. However, when dandelion grows in a polluted environment, it is known to take up, from both aerial and soil sources, many more trace metals than other plants.¹³⁵⁶ Thus, TE content in plants used for herbal medicaments should be of special concern (Lesniewicz et al., 2006). Ernst (2002) reported that Asian herbal medicines have elevated contents, mainly of Hg, Pb, and As, possible due to several factors: (1) plants sampled from polluted soils, (2) contamination during manufacture, and (3) intentional addition for alleged medicinal properties. Popular herbal tea in Thailand contains variable amounts of trace metals, of which Cd was detectable at concentration of >0.3 mg/kg and Pb at >20 mg/kg (Nookabkaew et al., 2006). Black teas from India contain the following levels of metals (mean, mg/kg): Cd, 0.14; Cr, 4.76; Cu, 24.07; and Ni, 2.53 (Seenivasan et al., 2008). The accumulation of metals in tea leaves is of a real concern because long-term tea plantation resulted in increased SOM, decreased pH, and elevated mobilization of most TEs (Zhang and Fang, 2007). These authors reported the highest trace metal concentrations in tea leaves as follows (mg/kg): Cd, 0.06; Cr, 0.43; Cu, 12.8; Ni, 3.13; Pb, 1.56; and Zn, 17.2.

Hyperaccumulators are plants and/or genotypes that accumulate metals above certain concentrations in leaves. As Greger¹³¹⁶ presented, based on a literature review, hyperaccumulators should contain trace metals in leaves above the following levels (mg/kg):

- >100—Cd
- >1000—Co, Cu, Ni, Pb
- >10,000—Mn, Zn

In polluted regions, some plants (not hyperaccumulators) may concentrate metals at those levels. Therefore, increased levels of a given metal in a hyperaccumulating plant must be related to their contents in other plants grown in the same environment.¹³⁵⁶ Plant-specific differences is common in the absorption of TEs by plants. This is supported by studies conducted by Overesch et al. (2007), indicating that among plants growing on polluted and acid floodplain soils at the Elbe river (Germany), *Artemisia vulgaris* concentrated Cd, Cu, and Hg; *Phalaris arundinaceae*—Ni, Pb, and Zn; and *Alopecurus praeensis*—As.

The best known and widely studied for its properties to accumulate high concentrations and tolerate toxic levels of Zn and Cd (partly Ni) in soils is *Thlaspi caerulescens*. Milner and Kochian (2008) consider this plant as a useful model system to study the micronutrient homeostasis and to elucidate the molecular, genetic, and physiological systems of hyperaccumulating plants. Other, especially endemic, plants growing in specific geochemical regions, also are recently intensively studied. Mesjasz-Przybyłowicz et al. (2004) analyzed contents of Ni and other trace metals in the leaves of *Berkheya coddii* from Ni-enriched ultramafic soils in South Africa. The concentration of Ni in leaves (18,000 mg/kg) exceeded several times its content of soil (1300 mg/kg) without any symptoms of toxicity.

The chemical composition of plants reflects, in general, the elemental composition of growth media. The extent to which this relationship exists, however, is highly variable and is governed by many different factors. The common concentrations of TEs in plants growing on various, but unpolluted, soils show quite a large variation for each element.

Behavioral properties of TEs in soil media influence their availability to plants, are as follows:

- Ag, Cr, Sn, Ti, Y—very slightly soluble in soil solution and not easily taken up by plants.
- As, Hg, Pb, F—relatively strongly sorbed by soil particles and not readily transported to above-ground parts of plants.
- B, Co, Cu, Mn, Mo, Ni—mobile in soil and readily taken up by plants.
- Cd, Se, Zn—very mobile in soil and easily bioaccumulated by plants.

It is observed with some regularity that sea plants contain more Al, As, Br, Cl, I, Sr, V, and Fe (on a dry matter basis) than terrestrial plants.^{1333a} This is thought to be a general rule in chemical element distribution among sea and terrestrial plants that has also been emphasized by Dobrovolsky,¹²⁸⁰ who calculated the variable abundance of TEs that are involved in biogeochemical cycling in different climatic zones of the globe. Kuehnelt et al., 2000 found in aquatic plants various organoarsenic species (different methylated compounds). Apparently this causes a higher As concentration in marine plants than in terrestrial ones.

II ABSORPTION

The main sources of TEs in plants are their growth media, for example, nutrient solutions or soils. Plants also may absorb TEs by above-ground parts from aerial deposition. One of the most important factors that determine the biological availability of a TEs is its binding to soil constituents. In general, plants readily take up the species of TEs that are dissolved in the soil solutions in either ionic or chelated and complexed forms. Much has been written on the absorption of TEs from solutions by Moore,⁵⁴⁸ Loneragan,⁴⁸⁹ Mengel and Kirkby,⁵³¹ Wild and Jones,¹¹⁸⁴ and others, and this absorption can be summarized as follows:

- It usually operates at very low TEs concentrations in solutions
- It largely depends on the concentrations in the solution
- The rate depends strongly on the occurrence of H⁺ and other ions
- The intensity varies with plant species and stage of development
- The processes are sensitive to some properties of the soil environment such as temperature, aeration, and pH and Eh
- It may be selective for a particular ion
- The accumulation of some ions can take place against a concentration gradient
- Mycorrhizae play an important role in TE cycling between external media and roots

Generalizations of plant processes operative in the absorption of TEs rest on the evidence for one or a few of the elements, and most often can represent some approximation to processes acting in a natural plant-soil system. Absorption by roots is the main pathway of TEs to plants; however, the ability of other tissues to readily absorb some nutrients, including TEs, has also been observed. The uptake of TEs by plants is affected, in addition to plant-specific ability, by soils factors, of which the most significant are pH, Eh, water regime, clay content, SOM, CEC, nutrient balance, and concentration of other TEs. Also, climatic conditions are shown to influence the rate of TEs uptake, which may be partly an indirect impact due to the water flow phenomenon. Generally, a higher ambient temperature influences a greater uptake of TEs by plants. McGrath et al. (2007) reported drastic decreases of Cu, Zn, and Fe contents of wheat grain over the last 160 years due to new varieties and increased yield.

Plant ability to take up chemical elements from growth media is evaluated by a ratio of element concentration in plants to element concentration in soils and is called Biological Absorption Coefficient (BAC), Index of Bioaccumulation (IBA), or Transfer Factors (TF). Some elements are more susceptible to phytoavailability than others (Figure 5.1). BAC values may highly vary, as for

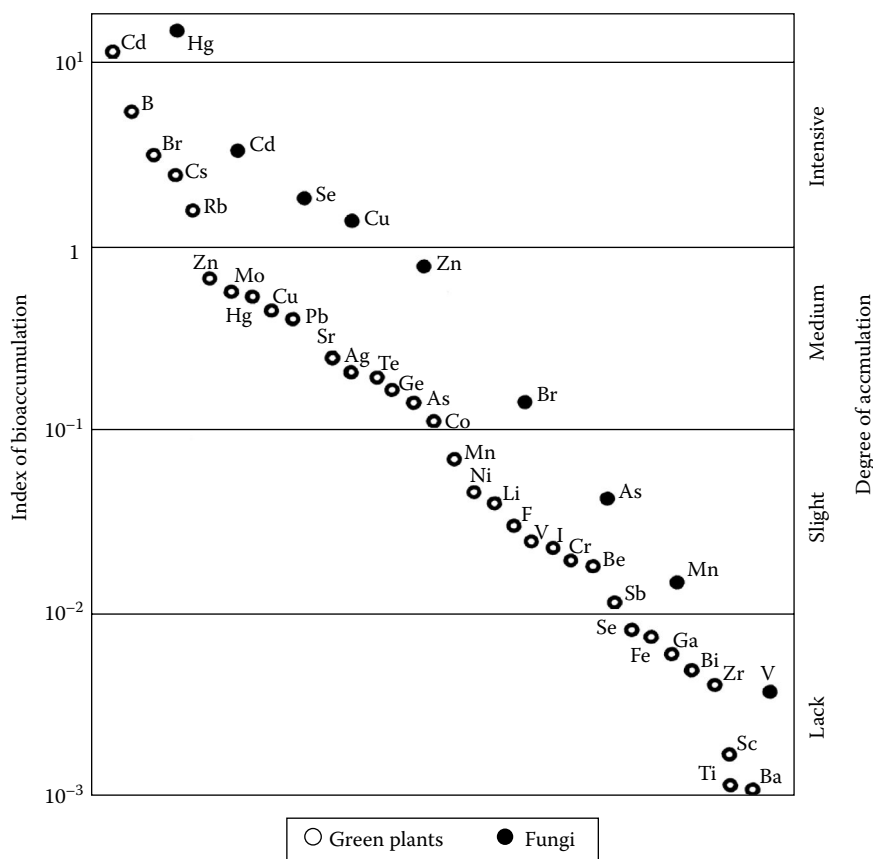


FIGURE 5.1 Bioaccumulation of trace elements by plants from soils. Index of bioaccumulation (BAC, IBA) was calculated as the ratio of trace elements in plants to their concentration in soils. The calculation is based on data for different plants and soils. Values for fungi are based on data from Byrne and Ravník (Reprinted from Byrne, A. R. and Ravník, V., *Sci. Total Environ.*, 6, 65, 1976. With permission.)

example among trees (*Populus nigra* L., *Platanus orientalis* L., *Laurus nobilis* L., *Pinus picea* L): from 209 to 2000 for Cu and from 10 to 1000 for Ni (Bini et al.¹²²⁶).

Transfer factor (TF) value may vary considerable for some parts of plants, as it is calculated for wheat grain: Pb, 0.0004; As, 0.008; Ni, 0.01; Cu, 0.02; Mn, 0.06; Se, 0.06; B, 0.14; Cd, 0.19; and Zn, 0.38.

A ROOT UPTAKE

The absorption of TEs by roots can be both passive (nonmetabolic) and active (metabolic), but there are some disagreements reported in the literature concerning which method is involved in certain elements. Despite controversies, in each case the rate of TE uptake will positively correlate with its available pool at the root surface. The crucial mechanism in the root uptake is the path of elements through cell walls and in intercellular spaces of the cortex.

Passive uptake is the diffusion of ions from the external solution into the root endodermis. Active uptake requires metabolic energy and takes place against a chemical gradient. Several data support the suggestion that, at the concentration generally present in soil solutions, the absorption of TEs by plant roots is controlled by metabolic processes within roots.^{489,548,788} The ion activity in the solution is believed to be one of the significant factors that influence plant uptake of ions. Presumably, this is

an important factor when the uptake is active, but may not be important when the uptake is passive. Morel (1997) described that at low external cation concentration in the soil solution ($<0.5 \mu\text{M}$), active absorption predominates, whereas at higher concentrations ($>0.1 \text{ mM}$) the absorption is dominated by passive processes.

Mechanisms of uptake differ, depending on the given element. Pb and Ni are preferably absorbed passively, while Cu, Mo, and Zn are preferably absorbed actively. When biological and structural properties of root cells are altered, however, all elements are taken up passively. This is the case when concentrations of elements pass over a threshold value for a physiological barrier.

Much evidence indicates that roots exhibit great activity in the mobilization of TEs that are bound by various soil constituents. Roots and associated microorganisms are known to produce various organic compounds which are very effective in releasing the TEs from firmly fixed species in soil. The TE most readily available to plants are in general, those that are adsorbed on clay minerals (especially, montmorillonite and illite), while those fixed by oxides and bound onto microorganisms are much less available. The depletion of TEs in solution from the root-soil interface reflects a higher rate of their uptake by roots than mass-flow and diffusion mechanisms in certain soils.^{531,638} The mechanisms of uptake of TEs by roots involve several processes: (i) cation exchange by roots, (ii) transport inside cells by chelating agents or other carriers, and (iii) rhizosphere effects.

Specific physical and chemical properties of the rhizosphere controlled by root exudates and microflora govern processes of the absorption of chemical elements. Root exudates, composed mainly of various organic compounds, control cation and oxyanions complexation and therefore play a key role in various processes that occur in the rhizosphere: (i) variation in pH and Eh regimes, (ii) mobility of macro- and micronutrients, and (iii) formation stable complexes (e.g., Fe-plaque) (Hinsinger et al., 2006). Root exudates of plants are composed mainly of amino acids, carboxylates, and other organic compounds, and vary with plant species (and varieties), microorganism association, and conditions of plant growth. Cation oxidation states around roots are believed to be of a great importance in these processes. Changes in the pH and Eh of the root ambient solution may play an especially significant role in the rate of availability of certain TEs.²⁴¹ Some root exudates (e.g., phytosiderophore 29-deoxymugineic acid) of metal-deficient cereal plants (e.g., Zn, Fe) are especially effective in mobilizing these metals from various precipitations within the root media.^{1004a}

Roots can also act as a “barrier” in the uptake or transport of TEs. Otte et al.¹¹⁰⁷ described interesting properties of roots of the plants (e.g., *Spartica anglica*) growing in marsh. The Fe-plaque formed on the roots consists mainly of Fe (hydroxides) with a large capacity to adsorb metals. Above certain threshold concentrations, the Fe-plaque becomes saturated with the trace metal, and the root is confronted with higher metal contents exceeding that of the surrounding medium. Chaney et al.¹²⁸ believed that the reduction step is obligatory in root uptake of Fe. The reduction of other metals such as Mn, Cu, Sn, or Hg in the uptake step apparently has not been clearly observed. Rice roots, on the other hand, exhibit a peculiar mechanism to absorb Si and Se in the form of oxides.³⁹⁵ Roots of plants grown in metal-contaminated sites can develop mechanisms to protect the plant from excessive uptake of a metal (Santa-Maria and Cogliatti, 1998). However, roots from several hyperaccumulating plants do not enhance metal mobilization (Zhao et al., 2001). Ozaki et al. (2005) observed effects, either inhibition or enhancement, depending on the reaction with the functional groups outside the cells in roots. In general, the presence of Ca in solution enhances the selectivity in the uptake of metabolically important elements against unwanted ones, especially Y and lanthanides.

The ability of different plants to absorb trace elements varies greatly; when compared on a large scale, however, the index of their accumulating ability illustrates some general trends. Some elements such as Cd, B, Br, Cs, and Rb are extremely easily taken up, while Ba, Ti, Zr, Sc, Bi, Ga, and to an extent, Fe and Se, are but slightly available to plants (Figure 5.1). This trend, however, will differ a great deal for particular soil–plant systems. Marked differences in the metal uptake between both plant species and varieties open up new aspects for plant breeding programs for the biodepletion in metal transport to the food chain. Also, there are experiments carried out on increasing the uptake

of Zn and Fe in wheat grown on soils with low contents of these metals. Chelating agents, EDTA and EDDS, added to soil increased the absorption of these metals by wheat but inhibited their translocation from shoots to grains (Nowack et al., 2008).

Fungi are nongreen plants with quite a diverse mechanism of nutrient uptake, and they have a specific affinity for some trace elements. They may accumulate Hg and also other elements such as Cd, Se, Cu, and Zn to high levels (Figure 5.1). Concentrations of several trace elements in plants from a pine forest in Japan indicate that there is a preferable uptake by mushrooms of such elements as Cd, Zn, Cu, Cs, and Rb.^{1564,1565} Concentrations of these elements were one order of magnitude higher than those in plants growing in the same forest. Concentrations of Ca and Sr in mushrooms, on the other hand, were lower than those in plants. Recent studies have indicated that some mushrooms may be considered as trace metal accumulators. Especially edible mushrooms have been analyzed, and results confirmed that most trace elements are concentrated in both caps and stalks of mushrooms (Falandysz et al., 2003; Yamac et al., 2007; Svoboda and Chrastny, 2008).

B FOLIAR UPTAKE

Foliar uptake is governed by several factors, mainly by surface properties of leaves and by aerial deposition of elements (contaminants). Elements absorbed by leaves are partly translocated to roots and are also leached from plant foliage, especially by acid rain. Under specific conditions, and especially with atmospheric pollution, a high proportion of trace metals may enter plant tissues. Dalenberg and van Driel^{1270s} have calculated that 73–95% of the total ²¹⁰Pb content of field crops are from aerial deposition on leaf surfaces.

The bioavailability of trace elements from aerial sources through the leaves may have a significant impact on plant contamination and it is also of practical importance in foliar applications of fertilizers, especially of elements such as Fe, Mn, Zn, and Cu. Foliar absorption of radionuclides released into the atmosphere from nuclear weapons testing and nuclear power installations is particularly of great concern.

Foliar uptake is believed to consist of two phases—nonmetabolic cuticular penetration, which is generally considered to be the major route of entry, and metabolic mechanisms, which account for element accumulation against a concentration gradient. The second process is responsible for transporting ions across the plasma membrane and into the cell protoplast. Wytenbach et al.¹⁵⁵³ studied the uptake of As, Br, and I by Norway spruce in order to distinguish between the uptake from soils and from gaseous or soluble compounds in the air. They found a strong positive correlation between the endogenous needle concentrations and the surface loadings, and also insignificant correlations with total soil concentrations of these elements.

Trace elements taken up by leaves can be translocated to other plant tissues, including roots where the excesses of some metals seem to be stored. The rate of trace element movement among tissues varies greatly, depending on the plant organ, its age, and the element involved. Results illustrated in Figure 5.2 show that Cd, Zn, and Pb absorbed by the tops of brome grass were not likely to move readily to the roots, whereas Cu was very mobile.

A fraction of the trace elements absorbed by leaves may be leached from plant foliage by rainwater. Differences in leaching of trace elements can be related to their function or metabolic association. For example, the easy removal of Pb by washing suggests that the metal was largely a superficial deposit on the leaf surface. In contrast, the small fraction of Cu, Zn, and Cd that can be washed off indicates a greater leaf penetration of these metals than was noted for Pb by Little and Martin⁴⁸² and Kabata-Pendias.³⁷⁴ Moreover, significant absorption of foliar-applied Zn, Fe, Cd, and Hg were reported by Roberts.⁶⁵⁷ Foliar leaching by acid rain may involve cation exchange processes, in which the H⁺ ion of rainwater replaces microcations held on binding sites in leaf cuticle.⁸⁸⁵

The absorption of trace metals, directly from wet (and dry) deposition by above-ground parts of plants, has been reported often. Morphology of the surface of leaves is an important factor governing foliar uptake of trace elements. Some plants (e.g., lichens, mosses, mushrooms, dandelion, etc.)

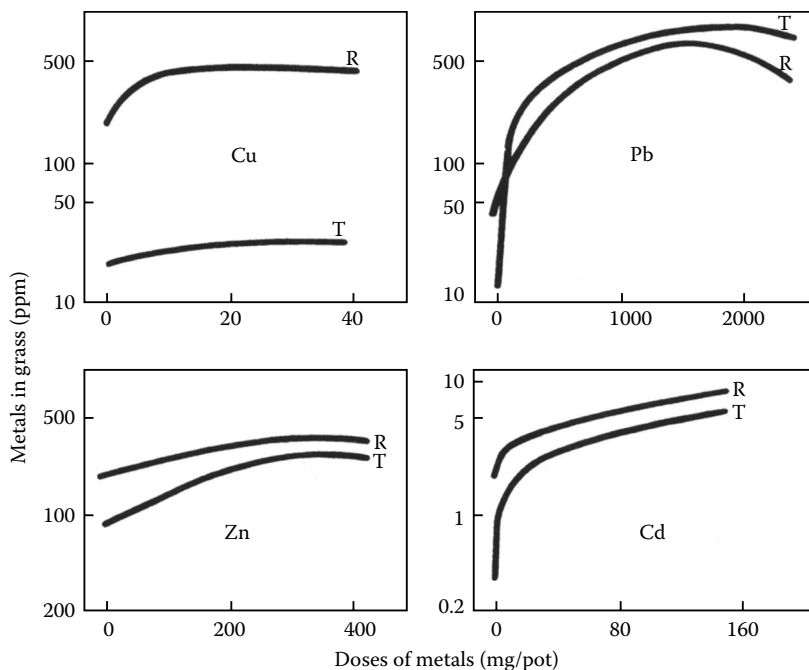


FIGURE 5.2 Distribution of trace metals from aerial sources between the tops (T) and roots (R) of brome grass. (Reproduced from Kabata-Pendias, A., *United Nations—ECE Symposium on Effects of Air-borne Pollution on Vegetation*, Warsaw, August 20, 134, 1979. © United Nations 1979. With permission.)

are especially susceptible to absorb elements and some compounds from aerial sources. Such plants are very suitable for the phytoindication of atmospheric pollution. Also, cereal tops show a relative sensitivity to aerial pollution, revealing the variation in trace metal contents (especially Pb and Ni) mainly due to the absorption from aerial particles (Figures 5.3 and 5.4).

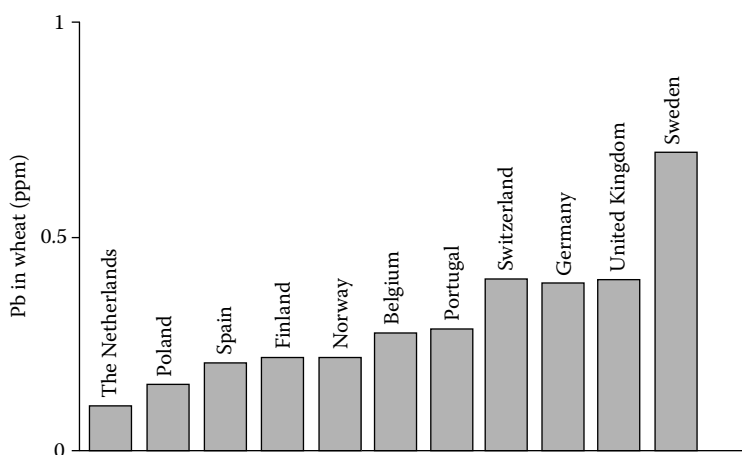


FIGURE 5.3 Geometric mean contents of Pb in winter wheat (*Triticum vulgare* L.) collected in 1985 from various countries in Europe. (FAO Cooperative Project Network on Trace Elements—Report, 1991, by M. Verloo *vide* Kabata-Pendias et al. (Reproduced from Kabata-Pendias, A., Piotrowska, M., and Dudka, S., *Plants as Biomonitors*, VCH, Weinheim, 1993, 485, Copyright Wiley-VCH Verlag GmbH & Co. With permission.)

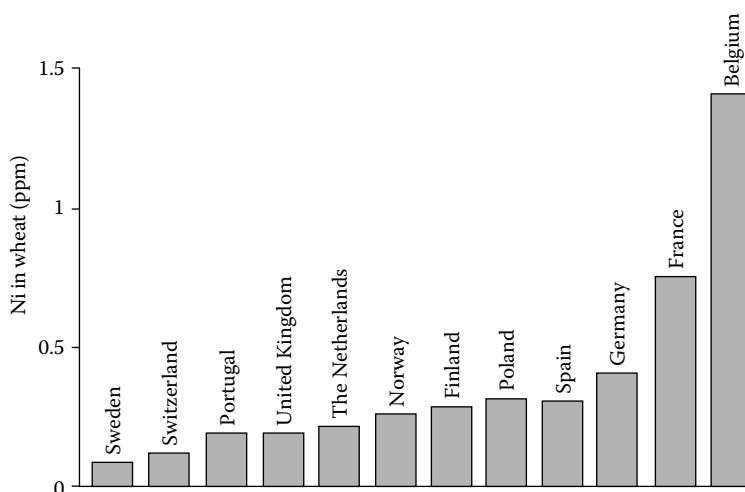


FIGURE 5.4 Geometric mean contents of Ni in winter wheat (*Triticum vulgare* L.) collected in 1985 from various countries in Europe. (FAO Cooperative Project Network on Trace Elements—Report, 1991, by M. Verloo *vide* Kabata-Pendias et al. (Reproduced from Kabata-Pendias, A., Piotrowska, M., and Dudka, S., *Plants as Biomonitors*, VCH, Weinheim, 485, 1993. Copyright Wiley-VCH Verlag GmbH & Co. With permission.)

III TRANSLOCATION

The transport of ions within plant tissues and organs involves many processes: (1) movement in xylem, (2) movement in phloem, (3) storage, accumulation, and immobilization. The chelating ligands are most important in the control of cation translocation in plants. However, numerous other factors such as pH, the oxidation–reduction state, competing cations, hydrolysis, polymerization, and formation of insoluble salts (e.g., phosphate, oxalate, etc.) govern metal mobility within plant tissues. The complexation of cations with organic acids (e.g., citric, malic, and amino acids) prevents their immobilization in the xylem and allows their transfer to the shoots. The immobilization of metals in roots due to various processes has a dominating impact on their translocation to the above-ground parts.

Tiffin⁷⁸⁸ gave a detailed review of the mechanisms involved in the translocation of TEs in plants. It can be summarized that long-distance transport of TEs in higher plants depends on the vascular tissues (xylem and phloem) and is partly related to the transpiration intensity. Chemical forms of TEs in phloem exudates differ for each element. Van Goor and Wiersma,⁸²² for example, reported that Zn was almost all bound to organic compounds, while Mn was only partly complexed.

The distribution and accumulation patterns of TE vary considerably for each element, kind of plant, and growth season. As reported by Scheffer et al.^{688a} in the phases of intensive growth of summer barley, the amount of Fe and Mn is relatively low, whereas the amount of Cu and Zn is very high. While the first two metals are accumulated mainly in old leaves and leaf sheaths, Cu and Zn seem to be distributed more uniformly through the plant. There are a number of publications on TE uptake and mobility in plants based on radionuclide experiments. Results are variable depending upon kind of experiment, plants, and other parameters. Shinonaga et al. (1999) reported that at foliar application on soybean plants, the most mobile transfer to seeds was observed for Rb, relatively mobile were Co and Se, and slightly mobile were As, Mn, Re, and Se. All other radionuclides studied were classified as immobile. The distribution of radionuclides in tomato plants was as follows: Co, Zn, Se, and Y—remained mainly in roots, Rb, Tc, and Re—were rapidly translocated into stems and leaves from roots (Shinonaga and Ambe, 2005).

Differentiation in TEs distribution between various parts of pine trees is also clearly shown by data presented in Table 5.1. A relatively common phenomenon, however, is the accumulation and

TABLE 5.1
Variation in Trace Element Contents in Pine Trees (mg/kg)

Plant Part	Al	B	Co	Cr	Cu	Fe	Mn	Ni	Pb	Ti	V
Needles											
1-year old	400	18.0	0.9	4.8	4.2	150	430	6.0	0.2	15	0.6
Older	200	24.0	0.8	4.0	2.5	370	740	2.1	0.5	30	1.2
Branches	400	6.0	0.6	1.6	3.0	650	430	1.1	0.6	25	1.8
Knots	120	4.5	0.2	0.8	1.2	78	185	0.3	0.1	6	0.8
Bark	230	4.5	0.4	1.0	2.0	100	123	0.4	0.3	15	2.8
Wood	7	0.9	0.1	0.3	0.6	5	61	0.3	0.1	1	0.2
Roots											
1-mm diameter	143	6.5	0.1	0.9	3.5	717	134	1.1	0.3	46	0.6
5-mm diameter	82	3.2	0.7	0.6	1.2	46	50	0.4	0.1	6	0.5

Source: Adapted from Dolobovskaya, A. S., *Pochvovedenie*, 3, 63, 1975 (Ru).

Note: Samples from the pine forest on old alluvial sands in Ukraine.

immobilization of trace metals in roots, especially when their metal supply is sufficient. The mechanism of exclusion seems also to control the transport of cations from roots to aerial parts.⁴¹⁷ Brundin et al.⁹⁵³ have shown that roots of plants growing along stream channels (mainly *Carex* species) as well as aquatic mosses are barrier-free with respect to trace metal uptake. However, physiological barriers are evident with respect to the transport of some metals (e.g., Cu, Zn, and Co) from roots to aerial parts. Most *Carex* species are barrier-free with respect to the translocation of Pb, and partly of Ni, Cr, and Mo.

Horiguchi and Nishihara¹⁰²⁸ studied the association of trace metals with the major constituents of potato tubers and peanut seeds. They found that only a small proportion of metals was distributed in the soluble components of a low molecular weight of peanut seeds, while potato tubers contained higher proportions of the metals in the low-molecular-weight fraction. It is presumed that starch as well as lipid fractions have only a weak affinity for trace metals, and that proteins are the major ligands that form complexes with metals in plants.

The transport of trace elements among plant organs also depends on the electrochemical variables of elements. In general, easily transported from roots to above-earth parts are Ag, B, Li, Mo, and Se; moderately mobile are Mn, Ni, Cd, and Zn; and strongly bound in root cells are Co, Cu, Cr, Pb, Hg, and Fe.

IV AVAILABILITY

The linear responses of TE absorption by several plant species in increasing their tissue concentrations from nutrient and soil solutions are illustrated in [Figure 5.5](#). These responses support the statement that more reliable methods in diagnosing the available trace element status of soils are those based on element concentrations in the soil solutions rather than methods based on the pool of soluble and/or extractable trace elements. The phytoavailability of trace metals correlates best with the concentration of cationic species in the liquid phase ([Table 5.2](#)).

A number of extraction methods have been suggested in recent years for the evaluation of trace element concentrations in soils. In general, they can be classified into separate groups as follows: acids (HCl, HNO_3 , aqua regia), chelating agents (EDTA, DTPA, TEA), buffered salt solutions (AAAc buffer), and unbuffered salt solutions (CaCl_2 , MgCl_2 , NaNO_3 , NH_4NO_3). Acid extractants,

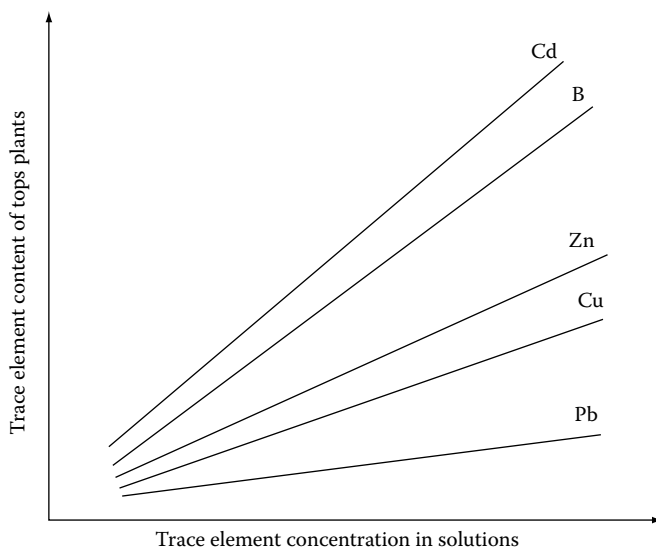


FIGURE 5.5 Trace element uptake by plants as a function of their concentrations in nutrient solutions.

depending on the strength and soil mineralogical composition, can extract nearly total amounts of trace metals. Chelating agents and buffered salt solutions are believed to extract potentially mobile portions of TEs. Neutral salt solutions have been introduced as simulating the natural soil solutions and therefore are useful to evaluate the ecological relevance of TEs.

Much work has been done on universal extractants for soil tests to assess micronutrient availability. Barber,⁹³⁰ Cox and Kamprath,¹⁵¹ Humez et al.¹³³⁹ and Walsh and Beaton⁸⁴⁷ prepared comprehensive reviews of chemical tests for the determination of water-soluble, acid-extractable, exchangeable, and complexed or chelated trace elements in soils.

A wide overview of trace element soil tests was recently presented in *Method of Soil Analysis*, edited by Bingham and Bartels.^{1225b} A number of papers also have been published on the widely applied sequential extractions for the determination of the operationally defined speciation or fractionation of trace metals what inform on their mobility and availability (see Chapter 3, Section 3.3.1). Good correlation was obtained for extracted and available metals added at elevated levels to the soils; whereas the correlation was less suitable for the prediction of plant-available quantities of metals under field conditions. Rieuwerts (2007) emphasized the specific conditions of tropical soils, particularly oxisols and ultisols, which reveal low activity of clays, low organic matter contents, low

TABLE 5.2
Relative Phytoavailability of Different Species of Metals from Soils

Metal Species	Phytoavailability
Simple or complex cations in solution phase	Easy
Exchangeable cations in organic and inorganic complexes	Medium
Chelated cations	Slight
Metal compounds precipitated on soil particles	Available after dissolution
Metals bound or fixed inside organic substances	Available after decomposition
Metals bound or fixed inside mineral particles (primary or secondary soil minerals)	Available after weathering and/or decomposition

pH values, and high levels of Fe oxides. Therefore, methods and data used for the prediction of metal phytoavailability in soils from the temperate climate regions cannot be adopted for these soils. Trace metals, mainly Cd, Cu, Zn, and Ni, in these soils appear to be mobile and thus easily bioavailable.

The interpretation of soil testing results is by no means an easy problem and may give reliable information for only a particular soil–plant system. These methods, nevertheless, are widely used, with various results, in agricultural practices. Minnich et al.¹⁰⁹⁴ stated that extraction procedures are easier and probably provide a better predictive ability for plant Cu uptake than Cu^{2+} activity measurements. The DTPA-extractable Cu and Zn correlated well with metal contents of plant tops.^{1047,1094} Minnich et al.¹⁰⁹⁴ emphasized that continual monitoring of soil solution ion activity or a buffering index is needed to improve predictions of plant ion uptake. The uptake of elements by plant roots is restricted to the liquid phase, therefore the content of metals in the soil solution is of primary importance.¹⁰⁴⁶ However, more information is needed about multiple ion activity ratios and about antagonistic or synergistic effects of accompanying cations and anions in the soil solution, in relation to uptake and physiological effects of trace metals in plants. Also, there is insufficient information on the availability of organic metal complexes in the solution phase.

The mixed extractant AAAC-EDTA was applied in the large world project on available trace element contents of soils in 30 countries, as carried out by Sillanpää and Jansson.¹⁴⁴¹ The relation between Cd, Pb, Co, and Se in crop plants and the pool of soluble forms of elements in soils, despite differences in soil variables and climatic conditions, was acceptably close. Schnug et al.¹⁴⁸² proposed *Coca Cola* as a relatively simple extractant and easily applied in soil testing procedures for mobile trace elements. The active compound in *Coca Cola* is phosphoric acid, which dissolves 27% of Fe, 38% of Cu, 86% of Zn, and 165% of Mn compared to those extracted by DTPA solution. Due to the relatively stable composition of *Coca Cola*, such an extractant might be suitable for specific experiments and projects.

The specific properties of plants are very significant in determining the bioavailability of trace elements and are quite variable with changing soil and plant conditions. The availability of different plant species to absorb certain trace elements from the same soil environment is illustrated in Table 5.3. In fact, different genotypes of the same species uptake different amounts of the trace elements. The wide variation (within the range of a factor of 100) in trace element contents of *Artemisia* species was observed in one meadow ecosystem.¹⁰⁹⁷ To provide an effective evaluation of the pool of bioavailable trace elements, therefore, techniques based on both soil tests and plant analyses should be used together.

Conditions of plant growth media also have a significant impact on the absorption of trace elements by roots. Findings of Miyasaka and Grunes¹⁴²¹ indicated that increasing the soil temperature from 8°C to 16°C influenced, by twofold higher, the contents of Cu, Zn, and Mn in leaves of winter wheat. Thus, during a cold season, plants may have low levels of some trace elements that may limit or affect their growth, and also cause a deficiency in grazing animals.

The sampling procedures for each field, each crop, and a specific plant part in the same stage of growth must be standardized for obtaining compatible results that could be classified as deficient, sufficient, or excessive and toxic for plants. Existing soil and plant tests, however, do not satisfactorily predict trace element deficiencies in crop plants that would respond to their application.

Ranges of TE concentrations and their classification for the mature leaf tissue presented in Table 5.4 are overall approximations and can differ widely for particular soil–plant systems. It is necessary to emphasize that ranges of concentrations of TEs required by plants are often very close to the content that exerts a harmful influence on plant metabolism. It is not easy, therefore, to make a clear division between sufficient and excessive quantities of trace elements in plants.

Houba and Uittenbogaard¹³³⁴ published results of determining 27 TEs in 140 plant kinds from 66 countries during the period from 1981 to 1993. Each plant kind was represented by a number of samples (a few tens) from various locations, and therefore it is difficult to interpret the variability in TE contents among plants. Some general trends, however, indicate that Pb is likely to be

TABLE 5.3
Variation in Trace Element Content among Various Plants from One Site in the Same Forest Ecosystem^a (mg/kg)

Plants	B	Cd	Cu	Fe	Mn	Pb	Zn	Cr	Ni
Grass	3.4	0.6	4.2	80	740	1.2	59	1.0	1.8
<i>Agrostis alba</i>									
Clover	9.0	0.7	6.0	115	136	2.8	99	1.0	2.2
<i>Trifolium pratense</i>									
Plantain	7.0	1.9	9.8	135	100	2.4	97	1.4	3.0
<i>Plantago major</i>									
Mosses									
<i>Polytrichum juniperinum</i>	3.4	0.8	9.2	800	176	22.4	69	2.0	2.0
<i>Entodon schreberi</i>	3.2	0.7	10.3	425	180	13.0	77	2.8	1.6
Lichens									
<i>Parmelia physodes</i>	2.4	0.4	5.0	1100	62	17.0	78	3.2	4.8
<i>Lobaria pulmonaria</i>	2.4	0.5	7.5	1450	66	28.0	74	3.2	2.4
Edible fungi									
<i>Cantharellus cibarius</i>	4.0	1.0	24.5	49	19	1.2	150	0.4	2.2
<i>Leccinum scabra</i>	0.8	2.7	18.0	44	6	<0.1	125	0.4	1.8
Inedible fungi									
<i>Tylopilus felleus</i>	3.5	1.6	35.0	50	14	0.4	180	0.4	1.2
<i>Russula veternosa</i>	6.4	1.0	32.0	28	18	1.0	175	0.4	1.0

Source: Adapted from Kabata-Pendias, A. and Wiacek, K., *Soil Sci. Ann.*, 36/4, 33, 1985.

^a Pine and birch forest on light sandy soil near Warsaw, Poland.

concentrated in cabbage and tomato leaves, Mo in sugar beet leaves and Chinese cabbage, Se in mushrooms, and Li in potato leaves. Onion bulbs contain elevated amounts of Cr, As, and Ni; lettuce leaves—Cr, Pb, and Cd; and spinach leaves—Li, Ni, and Pb.

V ESSENTIALITY AND DEFICIENCY

Study of the importance of certain TEs for health and development of plants began in the last century. At present, 17 trace elements (Al, B, Br, Cl, Co, Cu, F, Fe, I, Mn, Mo, Ni, Rb, Si, Ti, V, and Zn) are known to be essential for all plants, several are proved necessary for a few species only, and others are known to have stimulating effects on plant growth, but their functions are not yet recognized (Table 5.5). A feature of the physiology of these elements is that although many are essential for growth, they can also have toxic effects on cells at higher concentrations. Hypothetical schemes of the reactions of plants to increasing concentrations of the essential and nonessential trace elements are presented in Figure 5.6. The essential trace elements for plants are those which cannot be substituted by others in their specific biochemical roles and that have a direct influence on the organism so that it can neither grow nor complete some metabolic cycles. The elements needing more evidence to establish their essentiality usually are those thought to be required in very low concentrations (at µg/kg or ng/kg ranges) or that seem to be essential for only some groups or a few species of plants. An assessment of toxic contents and effects on plants is very complex since this depends on many factors both external and internal. Plants reveal a great behavioral plasticity under chemical stress. Based on a huge database of observations it has been possible to characterize soil properties that can affect deficiency of

TABLE 5.4
Approximate Concentrations of Trace Elements in Mature Leaf Tissue Generalized for Various Species (mg/kg)

Element	Deficient (if less than the stated amounts of essential elements)	Sufficient or Normal	Excessive or Toxic	Tolerable in Agronomic Crops ^{1081,1357}
Ag	—	0.5	5–10	—
As	—	1–1.7	5–20	0.2 ^a
B	5–30	10–100	50–200	100
Ba	—	—	500	—
Be	—	<1–7	10–50	—
Cd	—	0.05–0.2	5–30	0.05–0.5
Co	—	0.02–1	15–50	5
Cr	—	0.1–0.5	5–30	2
Cu	2–5	5–30	20–100	5–20
F	—	5–30	50–500	—
Hg	—	—	1–3	0.2 ^a
Li	—	3	5–50	—
Mn	10–30	30–300	400–1000	300
Mo	0.1–0.3	0.2–5	10–50	—
Ni	—	0.1–5	10–100	1–10
Pb	—	5–10	30–300	0.5–10
Se	—	0.01–2	5–30	—
Sn	—	—	60	—
Sb	—	7–50	150	—
Ti	—	—	50–200	—
Tl	—	—	20	—
V	—	0.2–1.5	5–10	—
Zn	10–20	27–150	100–400	50–100
Zr	—	—	15	—

Source: Data compiled from Bergmann, W. and Cumakov, A., *Diagnosis of Nutrient Requirement by Plants*, G. Fischer Verlag, Jena, and Priroda, Bratislava, 1977, 295 (Cz); Davis, R. D., Beckett, P. H. T., and Wollan, E., *Plant Soil*, 49, 395, 1978; Gough, L. P., Shacklette, H. T., and Case, A. A., *U.S. Geol. Surv. Bull.*, 1466, 1979, 80; Hondenberg, A. and Finck, A., *Z. Pflanzenernaehr. Bodenkd.*, 4/5, 489, 1975; Jones, J. B., *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI, 1972, 319; Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 1979, 300 (Po); Kitagishi, K. and Yamane, I., Eds., *Heavy Metal Pollution in Soils of Japan*, Japan Science Society Press, Tokyo, 1981, 302; Mengel, K. and Kirkby, E. A., *Principles of Plant Nutrition*, International Potash Institute, Worblaufen-Bern, 1978, 593.

Note: Values are not given for very sensitive or highly tolerant plant species.

^a FW basis.

some elements to crop plants (Table 5.6). The most common symptoms of micronutrient deficiency in sensitive plants are: (1) chlorosis and necrosis mainly of young leaves, (2) wilting, (3) melanism: brown, violet, red, (4) stunted growth, and (5) leaf deformation. Schematic plant response to changes in concentrations of essential and nonessential elements differs at the ranges of low contents (Figure 5.7).

Several models have been used to predict the bioavailability of trace metals, and in particular of Cd, Zn, Cu, and Pb (McLaughlin, 2001). These models, however, are limited to a given plant and specific growth conditions, and thus the application to crop plants and field condition is still

TABLE 5.5
Forms and Principal Functions of Trace Elements that are Essential for Plants

Element	Constituent of	Involved in
Al ^a	—	Controlling colloidal properties in the cell, possible activation of some dehydrogenases and oxidases
As ^a	Phospholipid (in algae)	Metabolism of carbohydrates in algae and fungi
B	Phosphogluconates	Metabolism and transport of carbohydrates, flavonoid synthesis, nucleic acid synthesis, phosphate utilization, and polyphenol production
Br ^a	Bromophenols (in algae)	—
Co	Cobamide coenzyme	Symbiotic N ₂ fixation, possibly also in non-nodulating plants, and valence changes stimulation synthesis of chlorophyll and proteins
Cu	Various oxidases, plastocyanins, and ceruloplasmin	Oxidation, photosynthesis, protein and carbohydrate metabolism, possibly involved in symbiotic N ₂ fixation, and valence changes, cell wall metabolism
F ^a	Fluoracetate (in a few species)	Citrate conversions
Fe	Hemo-proteins and nonheme iron proteins, dehydrogenases, and ferredoxins	Photosynthesis, N ₂ fixation, and valence changes
I ^a	Tyrosine and its derivatives (in angiosperms and algae)	—
Li ^a	—	Metabolism in halophytes
Mn	Many enzyme systems	Photoproduction of oxygen in chloroplasts and, indirectly, NO ₃ ⁻ in reduction
Mo	Nitrate reductase, nitrogenase, oxidases, and molybdoferredoxin	N ₂ fixation, NO ₃ ⁻ reduction, and valence changes
Ni ^a	Enzyme urease (in <i>Canavalia</i> seeds)	Possibly in action of hydrogenase and translocation of N
Rb ^a	—	Function similar to that of K in some plants
Se ^a	Glycine reductase (in <i>Clostridium</i> cells) combined with cysteine and methionine	Can replace S in some plants
Si	Structural components	—
Sr ^a	—	Function similar to that of Ca in some plants
Ti ^a	—	Possibly photosynthesis and N ₂ fixation
V ^a	Porphyrins, hemoproteins	Lipid metabolism, photosynthesis (in green algae), and, possibly, in N ₂ fixation
Zn	Anhydrases, dehydrogenases, proteinases, and peptidases	Carbohydrate, nucleic acid, and lipid metabolism

Source: Data compiled from Bowen, H. J. M., *Environmental Chemistry of the Elements*, Academic Press, New York, 1979, 333; Clarkson, D. T. and Hanson, J. B., *Annual Review of Plant Physiology*, Vol. 31, Ann. Reviews Inc., Palo Alto, CA, 1980, 239; Jagodin, B. A., et al. *Biologicheskaya Rol Mikroelementov i ich Primieneniye v Selskom Khozaystvie i Medicinie*, Nauka, Moscow, 1974, 329 (Ru); Mengel, K. and Kirkby, E. A., *Principles of Plant Nutrition*, International Potash Institute, Worblaufen-Bern, 1978, 593; Peyve, I. V., *Biologicheskaya Rol Mikorelementov i ikh Primeniye w Sielskom Khozaystvie i Medicinie*, Izd. Nauka, Moscow, 1974, 3 (Ru); Welch, R. M., *The biological significance of nickel, paper presented at Int. Symp. Trace Element Stress in Plants*, Los Angeles, November 6, 1979, 36.

^a Elements known to be essential for some groups or species and whose general essentiality needs confirmation.

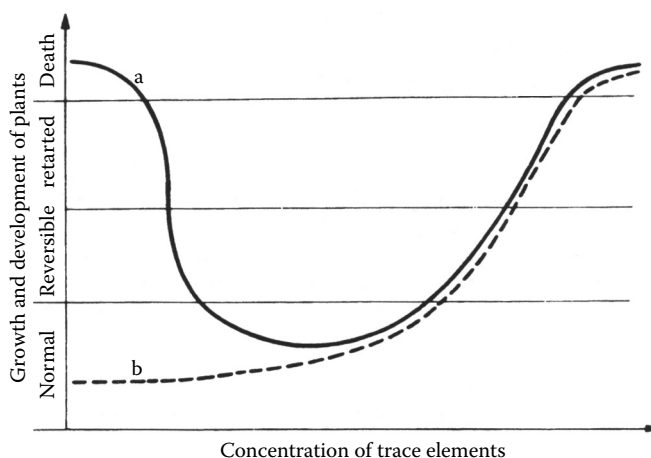


FIGURE 5.6 Schematic diagram of plant response to stress from deficiency and toxicity of trace elements: (a) essential trace elements; (b) nonessential trace elements.

uncertain. Bowen⁹⁴ classified the functions and forms of the elements in organisms, based on the current state of knowledge, by dividing the trace elements that occur in plants into the following groups:

- Elements incorporated into structural materials—Si, Fe, and rarely Ba and Sr.
- Elements bound into miscellaneous small molecules, including antibiotics, and porphyrins—As, B, Br, Cu, Co, F, Fe, Hg, I, Se, Si, and V.
- Elements combined with large molecules, mainly proteins, including enzymes with catalytic properties—Co, Cr, Cu, Fe, Mn, Mo, Se, Ni, and Zn.
- Elements fixed by large molecules having storage, transport, or unknown functions—Cd, Co, Cu, Fe, Hg, I, Mn, Ni, Se, and Zn.
- Elements related to organelles or their parts (e.g., mitochondria, chloroplasts, some enzyme systems)—Cu, Fe, Mn, Mo, and Zn.

The requirements of plants and even of individual species for a given micronutrient have been well-demonstrated by Hewitt³¹⁷ and Chapman.¹³¹ If the supply of an essential trace element is inadequate, the growth of the plant is abnormal or stunted and its further development, especially its metabolic cycles, are disordered. Although deficiency symptoms cannot be generalized, they may be quite characteristic for the particular element. Bergmann and Čumakov⁶⁶ presented comprehensive illustrations of deficiency (and some toxicity) symptoms in cultivars. The descriptions of deficiency symptoms summed up in Table 5.6 indicate that chlorosis is the most frequent symptom. Visible symptoms are important in diagnosis of deficiencies; however, disturbance of metabolic processes and consequent losses in production of biomass may occur before the deficiency symptoms are recognized. In order to develop a better diagnostic method, biochemical indicators based on enzymatic assays were proposed by Ruszkowska et al.⁶⁷² Rajaratnam et al.⁶³⁹ and Gartrell et al.²⁵⁸ as a sensitive test for a hidden deficiency of a given micronutrient. The activity of some enzymes is correlated mainly with Cu, Fe, and Mo levels in plant tissues. The practical use of the enzymatic assays is, however, greatly limited because of a high rate of variation and of technical difficulties in the determination of the enzymatic activity.

The most widely used diagnostic tests are soil and plant analyses. More specific diagnosis of critical levels of some trace metals in plant tissues should also be related to the ratio of antagonistic elements, as described by Nambiar and Motiramani⁵⁶⁰ for Fe:Zn ratios in maize. Concentrations of immobile TEs in old leaves or in whole plants, unlike those of mobile TEs, may be misleading in

TABLE 5.6
Symptoms of Micronutrient Deficiency in Some Common Cultivars

Element	Symptoms	Sensitive Crop
B	Chlorosis and browning of young leaves; killed growing points; distorted blossom development; lesions in pith and roots, and multiplication of cell division	Legumes, <i>Brassica</i> (cabbage and relatives), beets, celery, grapes, and fruit trees (apples and pears)
Cu	Wilting, melanism, white twisted tips, reduction in panicle formation, and disturbance of lignification and of development and fertility of pollen	Cereals (oats), sunflower, spinach, and lucerne (alfalfa)
Fe	Interveinal chlorosis of young organs	Fruit trees (citrus), grapes, and several calcifuge species
Mn	Chlorotic spots and necrosis of young leaves and reduced turgor	Cereals (oats), legumes, and fruit trees (apples, cherries, and citrus)
Mo	Chlorosis of leaf margins, “whiptail” of leaves and distorted curding of cauliflower, “fired” margin and deformation of leaves due to NO ₃ excess, and destruction of embryonic tissues	<i>Brassica</i> (cabbage and relatives) and legumes
Zn	Interveinal chlorosis (mainly of monocots), stunted growth, “little leaf” rosette of trees, and violet-red points on leaves	Cereals (corn), legumes, grasses, hops, flax, grapes, and fruit trees (citrus)

Source: Data compiled from Bergmann, W. and Cumakov, A., *Diagnosis of Nutrient Requirement by Plants*, G. Fischer Verlag, Jena, and Priroda, Bratislava, 1977, 295 (Cz); Bussler, W., *Int. Symp. Trace Element Stress in Plants*, Los angeles, November 7, 36, 1979; Mengel, K. and Kirkby, E. A., *Principles of Plant Nutrition*, International Potash Institute, Worblaufen-Bern, 1978, 593; Oelschäger, W. and Menke, K. H., *Über Selengehalte pflanzlicher, tierischer und anderer Stoffe, Sonderdruck Z. Ernährungswiss.*, 9, 208, 216, 1969.

assessing the nutrient status of plants. Nevertheless, plant tissue analysis has been used successfully for assessing deficiencies when based on the normal tissue contents for plant genotypes or species and organs and the stage of plant development. A comprehensive literature has been published in various countries on the diagnosis of trace element deficiencies and their correction through the application of particular micronutrients. Mengel and Kirkby⁵³¹ presented the most current information

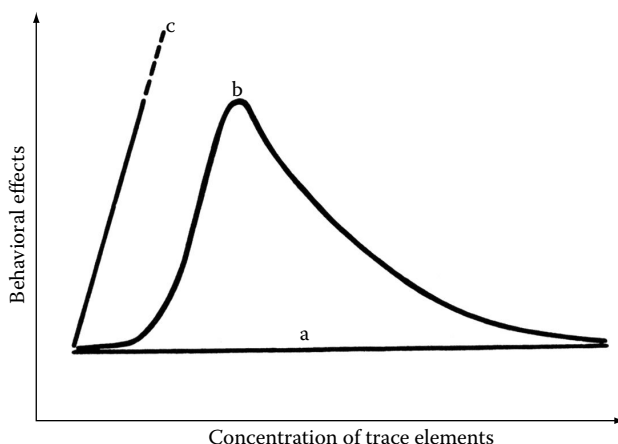


FIGURE 5.7 Schematic diagram of behavioral plasticity of plants under chemical stress: (a) no behavioral change of entirely tolerant species; (b) development of behavioral tolerance; (c) reaction of nontolerant species leading to damage of organisms followed by no recovery.

on micronutrients and indicated the need for their application to some cultivars. It should be emphasized, however, that the application of a given micronutrient is effective only if the soil content or the availability of the element is low. High-yield crop plants can suffer from acute or light deficiencies of some TEs. Finck⁹⁹⁵ gave an example of the extent of the deficiencies (both medium and light) in high-yield grain crops: (1) Mn supply to oats—on brown earths 40% and on calcareous marsh soils about 50% of fields, (2) Cu supply to oats—about 20% of fields on both soil types, and (3) Zn supply to wheat—about 15% of fields on both soil types.

Both deficiencies and toxicities of TEs for plants most commonly result from complex factors that vary with the specific environment. However, many observations and experiments conducted on various soil types in different countries have clearly demonstrated that soil genesis and soil properties are the main factors controlling TE deficiencies. The data summarized in Table 5.7 present the general relationship between the occurrence of micronutrient deficiencies in plants and soil properties. The most frequently occurring deficiencies are related to extremely acid soils (light sandy) or to alkaline soils (calcareous) with improper water regimes and with excesses of phosphate, N, and Ca, as well as Fe and Mn oxides.

VI TOXICITY AND TOLERANCE

Metabolic disorders of plants are affected not only by TEs, but also by their excesses. In general, plants are much more resistant to an increased concentration than to an insufficient content of a given element. Although many observations have been published on the harmful effects of trace element excesses, the nature of these processes is still poorly understood. Basic reactions, as reviewed by Peterson,⁶⁰⁹ Foy et al.²⁴¹ Bowen,⁹⁴ and Prasad and Strzalka,¹⁴⁶¹ related to toxic effects of element excesses are the following:

- Changes in permeability of the cell membrane—Ag, Au, Br, Cd, Cu, F, Hg, I, Pb, U.
- Reactions of thiol groups with cations—Ag, Hg, Pb.
- Competition for sites with essential metabolites—As, Sb, Se, Te, W, F.
- Affinity for reacting with phosphate groups and active groups of ADP or ATP—Al, Be, Sc, Y, Zr, lanthanides and, possibly, all other trace metals.
- Replacement of essential ions (mainly major cations)—Cs, Li, Rb, Se, Sr.
- Occupation of sites for essential groups such as phosphate and nitrate—arsenate, fluorate, borate, bromate, selenate, tellurate, and tungstate.
- The damage to photosynthesis apparatus involved in several metabolic alterations is the most significant effect of the excess of trace metals.

There are suggestions that metal-induced biochemical changes in plants are similar to responses elicited by pathogen attack.¹³⁷⁸ Despite the reported diversity in toxicity levels, it can be stated that the most toxic metals for both higher plants and certain microorganisms are Hg, Cu, Ni, Pb, Co, Cd, and possibly also Ag, Be, and Sn.

An assessment of toxic concentrations and effects of trace elements on plants is very complex because it depends on so many factors that it cannot be measured on a linear scale. Some of the most important factors are the proportions of related ions that are present in solution and their compounds. For example, the toxicity of arsenate and selenate is markedly reduced in the presence of excess phosphate or sulfate, and metallo-organic compounds may be either much more toxic than cations or much less so. It should also be noted that certain compounds (e.g., oxygenated anions of metals) may be more toxic than their simple cations. Van Assche and Glijsters¹¹⁷⁵ reported that enzyme measurements in plants (2-week-old test bean) can be a criterion for the phytotoxic effect of soil pollution with trace metals. The metal toxicity is reflected by the increase in capacity of various enzymes (e.g., peroxidase, dehydrogenase). The specific plant (iso)enzyme reactions on different

TABLE 5.7
Soil Factors Contributing to Micronutrient Deficiency

Element	Soil Units ^a	pH Range	Organic Matter	Water Regime	Other Factors	Critical Deficiency Limit in Soil ^b (mg/kg)	Plants Responding	Some Countries of Occurrence
B	Podzols, Calcisols, Gleysols, Nitosols, Ferralsols	Acid and neutral	Very low or very high	Flooded soils	Light texture, free CaCO ₃	0.1–0.3 (HW)	Beets, legumes, crucifers, and grapes	Australia, Egypt, France, Poland, Taiwan, U.S., Russia, China, India
Co	Podzols, Histosols, Calcisols, Planosols	Neutral, alkaline, or strongly acid	High	High moisture	Free CaCO ₃ , high Fe, and Mn	0.02–0.3 (AA) ^c	Legumes	Australia, France, Germany, Poland, Sweden, U.S., Russia
Cu	Histosols, Podzols, Calcisols, Planosols	—	Low or high	High moisture	Light leached soil, high N, P, and Zn, free CaCO ₃	1–2 (NA, 0.5 <i>N</i>) 0.8–3 (NA, 1 <i>N</i>) 0.8–1 (Ac-ED) 0.2 (AC)	Cereals, legumes, and citrus	Australia, Egypt, U.S., Russia, EU countries
Fe	Rendzinas, Ferralsols, Planosols, Chernozems	Alkaline	High with free CaCO ₃ or low in acid soil	Poor drainage, moisture extremes	Free CaCO ₃ , high P, Mn, and HCO ₃ ⁻	0.2–1.5 (DT) 2.5–4.5 (DT) <30–35 (Ac-ED)	Citrus, grapes, pineapples, and tomatoes	Throughout the world, and especially in arid and semiarid regions

Mn	Podzols, Calcisols, Histosols	Strongly acid or alkaline	High, e.g., alkaline peats	Moisture extremes	Free CaCO ₃ and high Fe	1–5 (DT) 20–100 (HR) 1–2 (AC) 14–70 (PA)	Cereals, legumes, beets, and citrus	Australia, France, U.S., Russia
Mo	Podzols, Ferralsols	Strongly acid to acid	—	Good drainage	High Fe, Al oxides, and S ²⁻	0.01–0.6 (AO) ^d <0.1 (HW)	Crucifers, cucurbits, and legumes	Australia, India, U.S., Russia
Se	Podzols, Histosols, Ferralsols	Acid	High	Waterlogging	High Fe oxides and S	<0.04 (T) ^c	—	Australia, U.S., some EU countries
Zn	Podzols, Calcisols, Planosols	Strongly acid or alkaline	Low	—	Free CaCO ₃ , high N and P	1–8 (HA) 1.5–3 (ED) 0.4–1.5 (DT) 0.3–2 (AC)	Cereals, legumes, and citrus	Australia, France, India, U.S., Russia

Note: Explanation of symbols used for extraction methods determining contents of soluble elements: AA, 2.5% acetic acid; AC, ammonium acetate; AO, ammonium oxalate; DT, DTPA; ED, EDTA; Ac-ED, ammonium acetate-EDTA; HA, 0.1 *N* hydrochloric acid; HR, hydroquinone reducible method; HW, hot water; NA, 0.5 or 1 *N* nitric acid; PA, 0.1 *N* phosphate acid; and T, total.

^a Generalized soil types assigned to soil units as given in Table 3.1.

^b Critical deficiency limits vary highly among plant species and soil kinds.

^c Animal response.

^d Highly pH dependent.

trace metals were observed. Mahmood et al. (2007) reported that excess of Cu is more toxic to seedlings of cereals than Pb and Zn. Wheat and rice seedlings are more susceptible to metal toxicity than barley.

Several orders of trace element toxicity to plants are presented in the literature and they vary with each experiment and each plant; however, they correlate fairly well with the following factors:

- Electronegativity of divalent metals
- Solubility products of sulfides
- Stability of chelates
- Bioavailability

Although plants adapt rather readily to chemical stress, they also may be very sensitive to an excess of a particular TEs. Toxic concentrations of these TEs in plant tissues are very difficult to establish. The values presented in Table 5.4 give very broad approximations of possibly harmful amounts of trace elements in plants. Visible symptoms of toxicity vary for each species and even for individual plants, but most common and nonspecific symptoms of phytotoxicity are chlorotic or brown points of leaves and leaf margins, and brown, stunted, coralloid roots (Table 5.8).

TABLE 5.8
General Effects of Trace Element Toxicity on Common Cultivars

Element	Symptoms	Sensitive Crop
Al	Overall stunting, dark green leaves, purpling of stems, death of leaf tips, and coralloid and damaged root system	Cereals
As	Red-brown necrotic spots on old leaves, yellowing or browning of roots, depressed tillering, wilting of new leaves	Legumes, onion, spinach, cucumbers, broomgrass, apricots, and peaches
B	Margin or leaf tip chlorosis, browning of leaf points, decaying growing points, and wilting and dying-off of older leaves In severely affected pine trees, necrosis occurs on needles near the ends of shoots and in upper half on the tree	Cereals, potatoes, tomatoes, cucumbers, sunflowers, and mustard, apple, apricots, citrus, and walnut
Be	Inhibition of seed germination and reduced growth, degradation of protein enzymes	—
Cd	Brown margin of leaves, chlorosis, reddish veins and petioles, curled leaves, and brown stunted roots Severe reduction in growth of roots, tops, and number of tillers (in rice) Reduced conductivity of stem, caused by deterioration of xylem tissues. Reduction of chlorophyll and carotenoids	Legumes (bean, soybean), spinach, radish, carrots, and oats
Co	Interveneal chlorosis in new leaves followed by induced Fe chlorosis and white leaf margins and tips, and damaged root tips	—
Cr	Chlorosis of new leaves, necrotic spots and purpling tissues, injured root growth	—
Cu	Dark green leaves followed by induced Fe chlorosis, thick, short, or barbed-wire roots, depressed tillering. Changes in lipid content and losses of polypeptides involved in photochemical activities	Cereals and legumes, spinach, citrus seedlings, and gladiolus
F	Margin and leaf tip necrosis, and chlorotic and red-brown points of leaves	Gladiolus, grapes, fruit trees, and pine trees
Fe	Dark green foliage, stunted growth of tops and roots, dark brown to purple leaves of some plants (e.g., “bronzing” disease of rice)	Rice and tobacco
Hg	Severe stunting of seedlings and roots, leaf chlorosis and browning of leaf points	Sugar beets, maize, and roses
Li	Chlorotic and necrotic spots on leaves and injured root growth	Citrus

TABLE 5.8 (continued)
General Effects of Trace Element Toxicity on Common Cultivars

Element	Symptoms	Sensitive Crop
Mn	Chlorosis and necrotic lesions on old leaves, blackish-brown or red necrotic spots, accumulation of MnO ₂ particles in epidermal cells, drying tips of leaves, and stunted roots and plant growth	Cereals, legumes, potatoes, and cabbage
Mo	Yellowing or browning of leaves, depressed root growth, depressed tillering	Cereals
Ni	Intervinal chlorosis (caused by Fe-induced deficiency) in new leaves, gray-green leaves, and brown and stunted roots and plant growth	Cereals
Pb	Dark green leaves, wilting of older leaves, stunted foliage, and brown short roots	—
Rb	Dark green leaves, stunted foliage, and increasing amount of shoots	—
Se	Intervinal chlorosis or black spots at Se content at about 4 mg/kg, and complete bleaching or yellowing of younger leaves at higher Se content, pinkish spots on roots	—
Ti	Chlorosis and necrosis of leaves, stunted growth	Beans
Tl	Impairment of chlorophyll synthesis, mild chlorosis and slight cupping of leaves, reduced germination of seeds and growth of plants	Tobacco and cereals
Zn	Chlorotic and necrotic leaf tips, intervinal chlorosis in new leaves, retarded growth of entire plant, and injured roots resemble barbed wire	Cereals and spinach

Source: Data compiled from Bergmann, W. and Cumakov, A., *Diagnosis of Nutrient Requirement by Plants*, G. Fischer Verlag, Jena, and Priroda, Bratislava, 1977, 295 (Cz); Foy, C. D., Chaney, R. L., and White, M. C., *Annu. Rev. Physiol.*, 29, 511, 1978; Greenland, D. J. and Hayes, M. H. B., Eds., *The Chemistry of Soil Constituents*, John Wiley & Sons, New York, 1978, 469; Kitagishi, K. and Yamane, I., Eds., *Heavy Metal Pollution in Soils of Japan*, Japan Science Society Press, Tokyo, 1981, 302; Mengel, K. and Kirkby, E. A., *Principles of Plant Nutrition*, International Potash Institute, Worblaufen-Bern, 1978, 593; Singh, M., Singh, N., and Bhandari, D. K., *Interaction of selenium and sulfur on the growth and chemical composition of raya*, *Soil Sci.*, 129, 238, 1980; Adriano, D. C., *Trace Elements in the Terrestrial Environment*, Springer-Verlag, New York, 1986, 533; Gettier, S. W. and Adriano, D. C., *Heavy Metals in the Environment*, Vol. 1, CEP Consult., Edinburgh, 1987, 472.

A common feature of plants is their ability to prolong survival under conditions of TE excesses in their environments, mainly in soils. Lower plants especially, such as microorganisms, mosses, liverworts, and lichens, reveal an extremely high level of adaptation to toxic concentrations of certain trace elements. Zajic,⁸⁹⁸ Weinberg,⁸⁵⁶ and Iverson and Brinckman³⁴⁴ presented comprehensive reviews on microorganisms involved in the cycling of trace metals and of their resistance to high metal concentrations. Tyler et al.¹¹⁷¹ reported that the depressions by 20–40% of most biological activities in forest litter/soil, compared to controls, were measured when concentrations of trace metals (Cu, Zn, and Pb) amounted to 2–10 times those of regional baseline samples. McGrath et al.¹⁰⁸⁹ found that the process of N-fixation is sensitive to increased concentrations of metals in soils. The inhibition by 50% of N-fixation by white clover rhizobium bacteria was at concentrations (mg/kg) of Zn, 334, Cu, 99, Ni, 27, and Cd, 10. These authors stated that mechanisms of the inhibition are still unknown and need to be investigated further, because the toxic effects can occur at metal concentrations close to or below the current guidelines for soil protection.

Although higher plants are believed to be less tolerant to increased concentrations of trace elements, they are also widely known to accumulate these elements and to survive on soils contaminated by large quantities of various TEs. Remon et al. (2007) suggested that metal tolerance is related to the ability to immobilize ions in roots and to enhance their transport to leaves. Antonovics et al.,³³ Peterson,⁶⁰⁹ Bradshaw,¹⁰¹ Woolhouse and Walker,⁸⁸⁶ and Tyler et al.¹¹⁷¹ attempted to summarize and define what is implied by the term “tolerance” of plants. This term refers to both the

population occurring in an area highly contaminated by TEs, and to individual plants or species which are able to withstand greater levels of toxicity than are others. Extreme tolerance of many species of bryophytes, lichens, and fungi is widely reported.^{1037,1171}

The trace-metal resistance in microorganisms and plants is of special concern. Practical problems and implications concerning metal-tolerant organisms can be related to:

- Microbial origin of metal ore deposits
- Metal cycling in the environment
- Geobotanical prospecting (i.e., the use of tolerant and sensitive plants to locate natural deposits of metal ores)
- Microbiological extraction of metals from low-grade ores
- Establishment of vegetation on toxic waste materials
- Microbiological treatment of waste waters
- Development of resistance in microorganisms to metal-containing fungicides and other pesticides

The evolution of metal tolerance is believed to be quite rapid in microorganisms and sometimes in vascular plants. As stated by Tyler et al.¹¹⁷¹ tolerant genotypes of some vascular plants may develop within a few years. Developed metal-tolerance of plants may be both phenotypically and genotypically acquired. Evolutionary changes caused by trace metals have now been recorded in a large number of species occurring on metalliferous soils that differ from populations of the same species growing on ordinary soils. Species of higher plants that show a tolerance to trace elements belong most commonly to the following families: Caryophyllaceae, Cruciferae, Cyperaceae, Gramineae, Leguminosae, and Chenopodiaceae. Balint et al. (2007) studied the influence of quantitative trait loci (QTL) on the tolerance to Cu and the accumulation of Cu, Fe, Mn, and Zn in wheat seedlings. QTL have variable impact that is associated with different chromosomes. Gonzalez-Mendoza and Zapata-Perez (2008) overviewed the cellular mechanisms involved in the tolerance to potentially toxic elements. These mechanisms include: (1) mycorrhizal association, (2) metal binding to cell wall, (3) precipitation by extracellular exudates, (4) reduction in uptake at the plasma membrane, (5) chelation by various peptides, and (6) compartmentation of metals in the vacuole. Pavliková et al. (2008) observed that changes in glutamate kinase activity is an reaction of spinach to increased levels of Cd and Zn in growth media.

The ranges of highest concentrations of trace elements found in various plant species are presented in Table 5.9. Various fungi are also well-known to be able to accumulate a high proportion of easily soluble and/or easily volatile elements such as Hg, Se, Cd, Cu, and Zn. The “upper critical level” of an element is the lowest tissue concentration at which it has toxic effects. Macnicol and Beckett¹⁰⁸¹ made an extensive survey of literature to establish critical levels of 30 elements, most predominant of which are Al, As, Cd, Cu, Li, Mn, Ni, Se, and Zn. The values established by these authors for the “upper critical levels” are quite similar to those presented by others as “excessive or toxic levels” (Tables 5.4 and 5.10). They stated that the critical levels for a given element are variable, which reflects both effects of interactions with other elements and developing plant resistance to a high tissue concentration of certain elements.

Microorganisms can very rapidly develop mechanisms of tolerance to excesses of trace metals. Fungi are usually more resistant than bacteria. Lichens reveal a relatively high tolerance to trace metals due to the presence of fungi hyphae. Fungi of mycorrhiza developed at the surface of roots of several plant species, mainly trees, can protect against the transfer of trace metals into root cells from surroundings. These phenomena are observed especially on trees in soil polluted with Cu and Zn.¹⁵²⁵ Turnau et al.¹⁵²⁴ observed in vacuoles of fungi hyphae (*Paxillus involutus*) granules with high contents of P, S, Ca, Al, and Cd. The Cd accumulation inside fungal vacuoles suggests the possibility of immobilization of metals by the symbiotic fungus. Hamon et al.^{1321a} reported that Cd and Zn in the rhizosphere of radish existed mainly as immobile forms complexed by organic compounds,

TABLE 5.9
The Greatest Accumulation of Some Metals (% AW) Reported in Various Plant Species

Element	Plant
>10%	
Ni	<i>Alyssum bertolonii</i>
Zn	<i>Thlaspi calaminare, caerulescens</i>
1–3%	
Cr	<i>Pimelea suteri</i> and <i>Leptospermum scoparium</i>
Co	<i>Crotalaria cobaltica</i>
Ni	<i>Alyssum bertolonii</i>
Se	<i>Astragalus racemosus</i>
Sr	<i>Arabis stricta</i>
U	<i>Uncinia leptostachya</i> and <i>Coprosma arborea</i>
Zn	<i>Viola calaminaria</i>
Mn	<i>Macadamia neurophylla</i>
0.1–1%	
Cu	<i>Becium homblei, Aeollanthus biformifolius</i>
Hg	<i>Betula papyrifera</i>
W	<i>Pinus sibiricus</i>
Zn	<i>Equisetum arvense</i>
Ni	<i>Berkheya coddii</i>
Pb	<i>Minuratia verna</i>

Source: Data compiled from Peterson, P. J., *Sci. Prog.*, 59, 505, 1971; Petrunina, N. S., *Problems of Geochemical Ecology of Organisms*, Izd. Nauka, Moscow, 1974, 57 (Ru).

TABLE 5.10
Critical Concentrations of Trace Metals in Plant Tissues (mg/kg)

Metal	Levels of Growth Depression	
	Insensitive Plant Species ¹⁰⁵²	For 10% Yield Loss ¹⁰⁸¹
As	—	1–20
Cd	5–10	10–20
Co	10–20	20–40
Cr	1–2	1–10
Cu	15–20	10–30
Hg	0.5–1	1–8
Ni	20–30	10–30
Zn	150–200	100–500

while dissolved Cd and Zn were largely uncomplexed in unplanted soil. The authors concluded that plants mainly absorb the free metal ions from soil solution.

Toxicity of trace metals to microorganisms and microbial processes in agricultural soils has been extensively reviewed by Giller et al.¹³¹⁰ The authors emphasized that the results of numerous laboratory ecotoxicological studies are the most difficult to meaningfully extrapolate to evaluate data on toxic effects that are likely to occur in the field.

A concept of “metal (Mn) equivalent” (related to “Zn equivalent” of trace metals to crop plants) in the toxicity to soil respiration has been proposed by Saviozzi et al.¹⁴⁸⁰ and is calculated as the sum of the amounts of the available metals, and related to the least toxic one: Mn equivalent = Mn + 1.95 Pb + 2.1 Ni + 2.5 Zn + 6.7 Cd + 6.7 Cu. Thus, Pb, Ni, and Zn show about twice and Cd and Cu about seven times the toxic effects of Mn.

Mechanisms of trace element resistance in plants have been the subject of several detailed studies which indicated that both highly specific and multiple metal tolerance may appear, as reported by Antonovics et al.,³³ Bradshaw,¹⁰¹ Simon,⁷²⁸ Foy et al.,²⁴¹ and Cox and Hutchinson.¹⁴⁹ These authors summed up possible mechanisms involved in metal tolerance. They distinguished external factors, such as low solubility and mobility of cations surrounding plant roots, as well as effects of metal ion antagonisms. The real tolerance, however, is related to internal factors. This is not a mechanism of tolerance in a simple sense, but consists of several metabolic processes:

- Selective uptake of ions
- Decreased permeability of cell walls or other differences in the structure and function of membranes
- Immobilization of ions in various organs (synthesis of immobilizing compounds including the formation of minerals, and/or fixation by charged ligands)
- Alteration in metabolic patterns—increased enzyme system that is inhibited, or increased antagonistic metabolite, or reduced metabolic pathway by passing an inhibited site, or decreased requirement for products of inhibited synthesis
- Adaptation to toxic metal replacement of a physiological metal in an enzyme
- Release of ions from plants by leaching from foliage, guttation, leaf shedding, and excretion from roots
- Release of volatile organic metal compounds (e.g., Hg, Pb, and Sn), mainly as methylated metals that are very toxic species to most organisms
- Excretion from leaf tips in the form of salts

In addition to the mechanisms mentioned, phenomena of avoidance of polluted substrates are reported. This is observed especially in the behavior of microorganisms which are capable of developing on better (less contaminated) substrate. Some vascular plants, while growing on topsoil heavily contaminated by trace metals, can develop roots in deeper soil layers.¹¹⁷¹

Selective uptake of ions is related to a capability of plants for active selective sorption and discrimination of available ions or compounds in the soil. Selective transport of ions to the tops taken up by roots is also observed. This selectivity depends most probably on immobilization mechanisms. Mechanisms of selective sorption and transport of trace ions can be broken down under a critical concentration of trace elements, and a passive flux of ions within a plant organism takes place (see Sections 5.2 and 5.3)

Decreased permeability of cell walls is closely associated with the immobilization. These mechanisms of the plant tolerance to metals (Al, Cd, Zn, Mn, and Pb) are broadly reviewed by Foy⁹⁹⁸ and Tyler et al.¹¹⁷¹ Binding to the cell wall, including wall impermeability, is observed in various vascular plants, bryophytes, lichens, fungi, and microorganisms. Several compounds such as thioneins, sulfides, pectic substances, and organic acids (e.g., uronic, mannuronic, norstictic—in lichens only) are involved in metal complexation. Thus, synthesis of immobilizing compounds and/or fixation by charged ligands are responsible for the removal of trace ions from plant metabolism by deposition

(storage) in fixed and insoluble forms in various organs and organelles. Roots are the most common storage for the excess of trace metals, but also foliage and seeds are known to accumulate deposited forms of different TEs. Tyler et al.¹¹⁷¹ stated that the immobilization in cell wall ligands is most probably a key reaction in reducing the toxicity of trace metal excess.

Kovalevsky^{1373,1374} reported that in old above-earth parts of plants, several mineral forms of trace elements can be distinguished; for example, FeAsS (arsenopyrite), ZnS (sphalerite), PbS (galena), MoS (molybdenite), HgS (cinnabar), and also some other trace element minerals, in the forms of carbonates, sulfates, fluorides, wolframites, etc. Other metals like Ag and Au were observed in the form of thin microscopic flakes (<2 μm). He reported that more than 30 elements can be temporarily excluded from physiological processes and stored in plant tissues as inactive minerals.

The biochemical resistance is not yet well-recognized, and may involve several other mechanisms of the immobilization. The alteration in metabolic patterns is related to an increase of the enzyme system that is inhibited, or to an increase of antagonistic metabolite. This also may be associated with a decreased requirement for products of the inhibited syntheses or with a reduction of metabolic pathways by passing an inhibited site of a part of the metabolic system. The great flexibility of enzymatic systems and variability among plant species are involved in the evolution of metal tolerance of which several points are still not clear. Considerable evidence was given by Antonovics et al.³³ and Cox and Hutchinson¹⁴⁹ that tolerant plants may also be stimulated in their growth by higher amounts of metal, which reveals a physiological need for an excess of a particular metal by a single plant genotype or species.

Tyler et al.¹¹⁷¹ discussed whether plants that become tolerant to trace metals may be equally productive as nontolerant species or populations. According to these authors the tolerance mechanism often imparts a demand for metabolic energy. Therefore, the growth of plants under the stress of elevated concentrations of trace metals is highly limited. In most cases, the morphology of those plants is altered, and salt excretion can be observed at the tips of leaves in some plants. In oats grown in soil heavily polluted with trace metals (mainly Zn and Pb), the composition of salt extraction was (in % of oven-dried weight): Zn 0.76, Pb 0.15, Mn 0.068, and Cu 0.039.¹³⁹⁹

The tolerance of some plants to elevated concentrations of trace metals in growth media and in tissues creates a health risk to humans and animals. This is a special problem in cases of TEs that are easily tolerated by plants and highly toxic to humans, as for example Cd. Therefore, health-related limits for certain elements in food plants are carefully controlled by national and international legislation. The contemporary limits can be changed in the future as more pertinent data are collected. Tolerant plants, due to their ability to grow in contaminated substrates, and due to the accumulation of extremely high amounts of TEs, may create a great health risk by forming a polluted link in the food chain.

The excess of TEs—both essential and nonessential to plants—has a deteriorating impact on metabolic processes. In some cases, toxic effects are specific for a given element (Table 5.8). Plants develop different mechanisms to protect against their excess. These mechanisms are, in general, related to the root (mainly root tips, meristems) exudates containing polygalacturonic acid that fix metals outside or within root cells, and to the production of phytochelates (various derivatives of glutathione) fixing metals and displacing either in vacuoles or on cell membranes.^{1459,1542,1551}

VII SPECIATION

Some TEs are involved in key metabolic events such as respiration, photosynthesis, and fixation and assimilation of some major nutrients (e.g., N, S). Trace metals of the transition metal group are known to activate enzymes or to be incorporated into metalloenzymes as electron transfer systems (Cu, Fe, Mn, and Zn) and also to catalyze valence changes in the substrate (Cu, Co, Fe, and Mo). Some particular roles of several TEs (Al, Cu, Co, Mo, Mn, and Zn), which seem to be involved in protection mechanisms of frost-hardy and drought-resistant plant varieties, are also reported.^{511,718}

A large variety of metal-binding ligands exist in plants, both within cells and in xylem and phloem. Depending on the size and physical and chemical characteristics, metals can form with ligands in plants either easily transported or strongly bound forms, and complexes. Both are of great metabolic importance because they control the transport of nutrients within the plant organs, and also protect the plant against an excess, especially of trace metals.^{1456,1459} Metal ions form complexes with small and macromolecular substances, mainly organic. Crucial are also microbial methylation processes that resulted in methylate-species of several elements, including trace metals.

Most metals form various complexes with both small and macromolecular organic compounds that are present in xylem and phloem of plants (Łobiński and Potin-Gautier, 1998; Schaumlöffel et al., 2003). Common chelating agents are organic acids (i.e., carboxylic, amino, mercaptic, mugineic, phytic), proteins, polysaccharides, lignins, pectins, DNA, metallothioneins, phytoferritins, and so on. Phytochelatins (oligomers of glutathione) act as chelators and play significant role in the transport and immobilization of trace metals. Their amount increases when the cell needs ligands to survive in an environment with high concentrations of metals. Several reviews have been recently published on structure, biosynthesis, and functions of phytochelatins (Leopold et al., 1999; Figuera et al., 2007; Navaza et al., 2008). Inorganic ligands such as Cl, F, and sulfate are also important complexants in plants (Prasad and Hagemeyer¹⁴⁶⁰).

According to Szpunar et al. (2003), general affinities of trace elements for complexation in biological systems are as follows:

- Ag, Cd, Cu, Hg, Zn—by proteins (*via* S)
- Co, Cu, Fe, Mn, Mo, Zn—by proteins (*via* O)
- Cr, Ni, Pt, Ru—by nucleic acids
- Ba, Cd, La, Pb, Sr—by polysaccharides
- Co, Fe, Ni, V—by terapyrrol ligands
- Al, Fe, NI—by small organic ligands

Plants are able to synthesize various metallo-complexes such as methylmercury, organoarsenic, and organoselenium (Schamlöffel et al., 2004). Relatively often selenomethionite has been found in wheat, soybean, and Se-enriched yeast (Shibita et al., 1992; Dauchy et al., 1994). Various organo-arsenic species (different methylated compounds) have been found in aquatic plants and apparently this causes a higher As concentration in marine plants than in terrestrial ones (Kuehnelt et al., 2000).

Organo-Pb species were of a special concern before the abatement Pb additives, into gasoline as an antiknock agent. Several Pb species, such as Me_3Pb^+ , $\text{Me}_2\text{Pb}^{2+}$, Et_3Pb^+ , Et_2MePb^+ , have been reported to be absorbed by plants through roots or by foliage from the atmosphere (van Cleuvenbergen and Adams, 1991).

The phytochelation of Cd and Cu has been demonstrated in cell cultures of rice, soybeans, and maize (Vacchina et al., 2000; Chassaigine et al., 2001). Pavliková et al. (2005) separated, using organic solvents and water, species of As, Cd, and Zn from spinach biomass. The highest proportion of As was extracted by water and identified as phytin, phytic acid, pectin, and metallothioneins. Zinc was extracted mainly by methanol and acidified (HCl) methanol; isolated fractions were: compounds with organic acids (including mugineic and phytic acids) flavone glucuronides, oligopeptides, proteins, lignins, and pectin. Cadmium was extracted predominantly by acidified methanol as fractions of: proteins, phytic acid, lignins, and pectin. However, the largest amount of Cd remained as nonextractable residues, mainly as polysaccharides.

VIII INTERACTION

A chemical balance in living organisms is a basic condition for their proper growth and development. Interactions of chemical elements are also of similar importance to deficiency and toxicity in

the physiology of plants. Interactions between chemical elements may be both antagonistic and synergistic, and their imbalanced reactions may cause a real chemical stress in plants.

Antagonism occurs when the combined physiological effect of two or more elements is less than the sum of their independent effects, and synergism occurs when the combined effects of these elements is greater. These interactions may also refer to the ability of one element to inhibit or stimulate the absorption of other elements in plants (Figure 5.8). All these reactions are quite variable and may occur inside the cells, within the membrane surfaces, and also surrounding plant roots. Interaction processes are controlled by several factors and these mechanisms are still poorly understood, although some data are available.^{241,581,840}

Interactions between major and TEs summarized in Table 5.11 clearly show that Ca, P, and Mg are the main antagonistic elements against the absorption and metabolism of several TEs. Some synergistic effects, however, have also been observed for antagonistic pairs of elements, depending on the specific reaction of the plant genotype or species.

Antagonistic effects occur most often in two ways—the macronutrient may inhibit trace element absorption and, in turn, the TEs may inhibit absorption of a macronutrient. These reactions have been observed especially for phosphate, but have also been reported for other macronutrients whose uptake and metabolic activity may be inhibited by several TEs.^{395,463}

Most important for practical application are the antagonistic effects of Ca and P on TEs such as Be, Cd, Pb, and Ni that often constitute a health hazard. Both major nutrients, Ca and P, are known

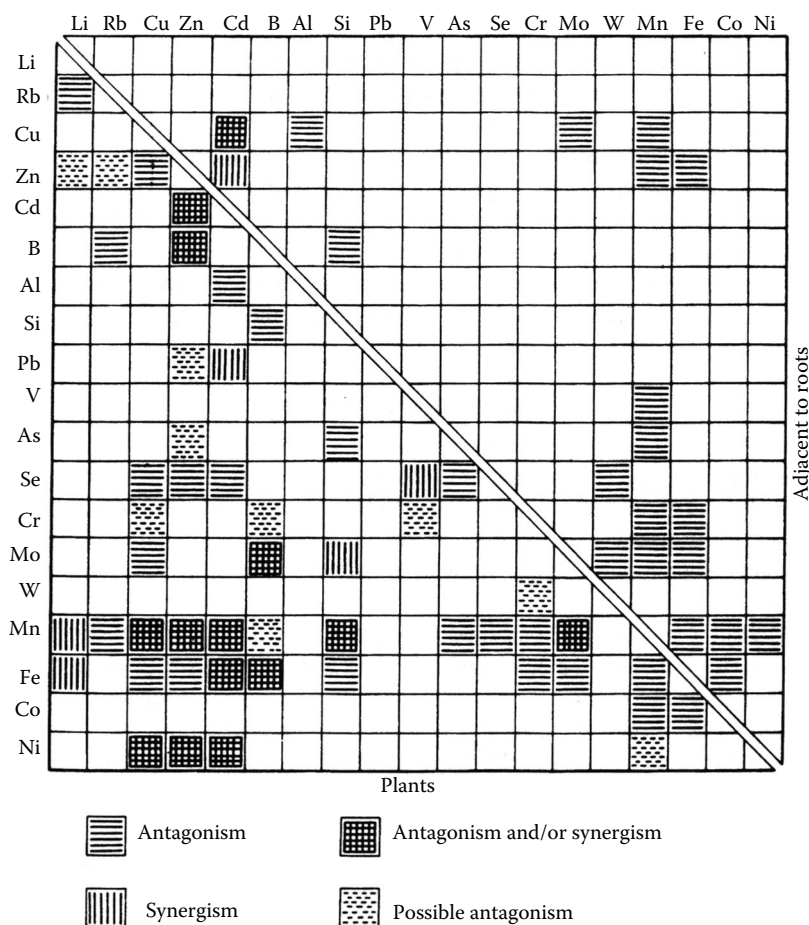


FIGURE 5.8 Interactions of trace elements within plant organisms and adjacent to plant roots.

TABLE 5.11
Interactions between Major Elements and Trace Elements in Plants

Major Element	Antagonistic Elements	Synergistic Elements
Ca	Al, B, Ba, Be, Cd, Co, Cr, Cs, Cu, F, Fe, Li, Mn, Ni, Pb, Sr, and Zn	Cu, Mn, and Zn
Mg	Al, Be, Ba, Cr, Mn, F, Zn, Ni ^a , Co ^a , Cu ^a and Fe ^a	Al and Zn
P	Al, As, B, Be, Cd, Cr, Cu, F, Fe, Hg, Mo, Mn, Ni, Pb, Rb, Se, Si, Sr, and Zn	Al, B, Cu, F, Fe, Mo, Mn, and Zn
K	Al, B, Hg, Cd, Cr, F, Mo, Mn, and Rb	—
S	As, Ba, Fe, Mo, Pb, Se, and Zn	F ^b and Fe
N	B, F, Cu, and Mn	B, Cu, Fe, and Mo
Cl	Br and I	—
Na	Mn	—
Si	B, Mn	—

Source: Data compiled from Gadd, G. M. and Griffiths, A. J., *Microb. Ecol.*, 4, 303, 1978; Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 1979, 300 (Po); Mengel, K. and Kirkby, E. A., *Principles of Plant Nutrition*, International Potash Institute, Worblaufen-Bern, 1978, 593; Mortvedt, J. J., soil reactions of Cd contaminants in P fertilizers, *Agron. Abstr.*, Dec. 3, 1978; Roques, A., Kerjean, M., and Auclair, D., *Environ. Pollut.*, 21, 191, 1980.

^a Reported for microorganisms.

^b Mutual pollution causes significant injury.

to play a significant role in the integrity of cell membranes, and therefore any imbalance in these nutrients may affect interaction processes either in nutrient solution external to or at the surface of root-cell membranes. It is noteworthy that although the antagonistic effects of P and Ca on many trace cations and anions are frequently reviewed in the literature, the antagonistic impact of Mg on trace metals is only occasionally studied. Ernst et al. (2008) reported that S metabolism in plants is affected by Cd and partly by Cu, whereas other metals/metalloids do not have any significant impact.

Deficiency of one TE essential to a plant can facilitate uptake of other micronutrients. The compensatory absorption of micronutrients under deficiency stress is reported for several elements and most commonly for Mn and Cu, and for Fe and Cu, Zn, and Mn.¹⁴⁶⁶ Antagonistic, additive, or synergistic, response of plants to binary mixtures of elements seems to be a concentration-dependent effect. It initially was observed by Chaney and Hornick¹²⁹ for the Cd/Zn relationship. Recent findings presented by Sharma et al.¹⁴⁸⁵ indicated that when only one element of binary mixtures, Cu/Cd, Cu/Zn, and Cd/Zn, exceeds some critical level of toxicity, the joint effect is either synergistic or additive. This clearly indicates that interaction effects are less metal-specific at high concentrations than at low metal concentrations.

Interrelationships between elements in different soils and/or plant species are of multivariant character. These relationships may be attributed to the ionic competition at the sorption sites of soil particles and also to properties of the surface root cell membrane and root exudates.

Interactions observed within plants between trace elements have also indicated that these processes are quite complex, being at times both antagonistic and synergistic in nature, and occasionally are involved in the metabolism of more than two elements (Figure 5.8). The greatest number of antagonistic reactions has been observed for Fe, Mn, Cu, and Zn, which are, obviously, the key elements in plant physiology (Table 5.5). These trace metals are linked to processes of absorption by plants and to the enzymatic pathway. The other TEs often involved in antagonistic processes with these four trace metals are Cr, Mo, and Se.

Synergistic interactions between TEs are not commonly observed. Those reported for Cd and other trace metals such as Pb, Fe, and Ni may be artifacts resulting from the destruction of physiological barriers under the stress of excessive concentrations of trace metals. Moreover, several reactions that occur in the external root media and affect root uptake should not be directly related to metabolic interactions, but the two reactions are not easily separated. Some interactions among trace metals are still unpredictable; for example, the addition of Ni (organic and inorganic forms) enhanced Cu, Zn, and Mn uptake by winter wheat, whereas the addition of Pb increased Cu and Zn.¹⁴⁴²

The greatest number of antagonistic reactions has been observed for Fe, Mn, Cu and Zn with several other elements, including As, Cr, Cr, Fe, Mo, Ni, Pb, Rb, and Se. Deficiency of one TE essential to a plant can facilitate uptake of other micronutrients. The compensatory absorption of trace elements under deficiency stress is reported for several elements and most commonly for Mn and Cu, for Fe and Cu, Zn, and Mn (Rengel et al.¹⁴⁶⁶). Broadly studied Cd/Zn, Cd/Cu and Cu/Zn relationships are very complex, and as Sharma et al. (1999) have described, when only one element of these binary ratios exceeds the toxic level, the joint effect is either synergistic or additive. There is a controversy regarding Cd/Zn interactions, however, Zn seems to play an important role in controlling the Cd uptake in Cd-contaminated soils, whenever the ratio Zn:Cd is higher than 100 (Kabata-Pendias and Terelak, 2004).

6 Elements of Group 1 (Previously Group Ia)

I INTRODUCTION

The trace alkali elements of Group 1 are: lithium (Li), rubidium (Rb), and cesium (Cs). The common characteristic of the alkali elements is a single electron in the outermost energy level, resulting in highly reactive chemical behavior. The relative bonding force holding these monovalent cations is presented most often in the order $\text{Cs}^+ > \text{Rb}^+ > \text{Li}^+$. These cations do not usually form complex ionic species, but can be bound in some chelates and organometallic compounds. Although their properties differ (Table 6.1) these lithophilic metals are relatively similar, especially Rb and Cs, in their behavior in crystallochemical and geochemical processes. They are closely associated with the major crustal components and are likely to enter silicate minerals.

II LITHIUM

A INTRODUCTION

Lithium is the lightest metal widely and relatively uniformly distributed through the Earth's crust but is likely to be concentrated in acidic igneous rocks and in argillaceous sedimentary rocks (Table 6.2). As highly reactive cation of relatively small ionic radii (Table 6.1) easily replaces in geochemical processes cations having sufficiently similar ionic radii: Mg^{2+} , Fe^{2+} , Al^{3+} , Ti^{4+} . Li is associated with minerals of the late pegmatitic stage, for example, micas (mainly biotite), some pyroxenes, and tourmalin, as well as with some sedimentary aluminosilicates, and phosphates. However, Li content in phosphorites is reported to be rather low, 1–10 mg/kg. Li is very mobile in geochemical processes and preferably enters silicate minerals rather than sulfide minerals. Common Li minerals, all associated with pegmatite bodies, are: petalite (Li, Na) $\text{AlSi}_4\text{O}_{10}$, spodumene $\text{LiAlSi}_2\text{O}_6$, and eucliptite LiAlSiO_4 .

Globally, mean Li content (mg/kg) in coals is 65, while the range in crude oil is 0.02–<3, and in benzene 0.001–<0.6 (Finkelman, 1999; Llorens et al., 2000).

Lithium is obtained mainly from spodumene (also from petalite). Estimated world Li production for 2008 was 27.4 kt (USDI, 2009). Li is used in organic synthesis, plastic production, and in ceramic and glass (mainly optic) manufactures. Extensive uses of Li are observed in batteries for video cameras, computers, telephones, and cordless tools. It is added to some rocket fuels and lubricants.

Lithium is also used in the pharmaceutical industry, in drugs for psychiatry and neurology. As a very soluble element, Li can become a serious water pollutant, especially with industrial sewage discharge.

B SOILS

During weathering Li is released easily from the primary minerals in oxidizing and acid media, and then is incorporated in clay minerals and Fe–Mn hydroxides, accumulated in phosphate rocks, and is also easily absorbed by organic matter. The Li content of soils is controlled more by conditions of soil formation than by its initial content in parent rocks. The Li distribution in soil profiles follows the general trends of soil solution circulation; however, it may be highly irregular.

TABLE 6.1
Selected Properties of Trace Elements of Group 1

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C) (g/cm ³)	Valence
Li, lithium	3	6.94	205	0.53	+1
Rb, rubidium	37	85.47	298	1.52	+1 ^b
Cs, cesium	55	132.91	334	1.87	+1

^a Approximately average values.

^b The oxidation states can also vary from +2 to +6.

The mean background Li contents for worldwide soils range from 13 to 28 mg/kg (Table 3.2). Mean Li abundance in soils indicates the lowest value for sandy soils (22 mg/kg), and the highest for heavy loamy (53 mg/kg) and calcareous soils (56 mg/kg). However, the lowest Li content (1.3) is in organic soil (Table 6.2). Surface soils of the Piedmont region of the southeastern United States contain Li from 11.5 to 33.3 mg/kg (four soil samples), and from the Coastal Plain, from 3.7 to 5.8 mg/kg (two soil samples). Higher contents of Li are in deeper soil horizons, and the greatest amount was found in the mother rocks, up to 59.9 mg/kg. Contents of soluble Li (extracted with 1 M NH₄Cl) in these soils are very low and do not exceed 3–5% of the total Li content in surface layers (Anderson et al., 1988).

In the arid climatic zones, Li follows the upward movement of the soil solution and may precipitate at top horizons along with easily soluble salts of chlorites, sulfates, and borates. These reactions explain a relatively higher Li content of soils such as solonchaks, solonetz, kastanozems, and prairien soils. Also, intrazonal young soils derived from alluvium reveal elevated Li concentrations. The Li content in mineral surface soils of Poland is highly and positively correlated with clay fraction. Its median values (of about 100 samples for each textural soil group) increase in the following order (in mg/kg): sandy light soils 3.8, light loamy soils 5.8, medium loamy soils 8.8, and heavy loamy soils

TABLE 6.2
Abundance of Trace Elements of Group 1 in Rocks and Soils (mg/kg)

Rock/Soil	Li	Rb	Cs
Earth's crust	20–25	90–110	<1–6
Igneous rocks	20	90	4
Mafic	0.5–10	20–45	0.5–1.5
Acid	15–40	100–200	2–5
Sedimentary rocks			
Argillaceous	50–75	120–200	5–10
Sandstones	10–40	10–45	0.5–2
Calcareous	2–20	5–30	0.5–2
Soils ^a	32	50	7.5
Arenosols (sandy)	5–70 (22) ^b	30–50	0.8–30 (5)
Podzols (medium loamy)	2–130 (46)	100–120	2.5–20 (8)
Cambisols (heavy loamy)	9–175 (53)	55–140	5–20 (10)
Calcisols (calcareous)	6–105 (56)	—	5–15 (8)
Histosols (organic)	0.01–3 (1.3)	10–20	—

^a Soil groups are given according to the WBR (Table 3.1).

^b Arithmetic means are given within parentheses.

12.9.¹³⁵¹ Average Li content in reference soils of the United States is 33 mg/kg and in soils of China, it is 35 mg/kg.¹³¹³ Geometric mean Li content in surface Venezuelan soils varies from 2.0 to 13.9 mg/kg upon different transection near the Caribbean shore.¹²⁷³ According to Kabata-Pendias and Krakowiak¹³⁵⁶ the texture of mineral soils is the most significant factor controlling the Li status in soils while all other parameters, such as SOM, CEC, and pH are of much less importance.

In the initial processes of soil formation, Li seems to be highly mobile, while later it may become more stable due to its firm bonding with clay minerals.⁸⁶⁴ However, as Shakuri⁷¹³ reported, water-soluble forms of Li in the soil profile reach up to about 5% of the total soil content and therefore Li is likely to occur in ground waters of areas having elevated Li contents in rocks and soils. Exchangeable soil Li is reported to be strongly associated with Ca and Mg.¹⁶⁴ Huh et al. (2004) examined the pedogenic behavior of Li and its isotopes during basalt weathering (in Hawaii) and suggested that in arid and subhumid sites heavier Li isotope is added from marine aerosol, whereas under greater rainfall there is a net loss of Li, and light Li isotope is likely to retained in weathered crust.

C PLANTS

The soluble Li in soils is readily available to plants; therefore, the plant content of this element is believed to be a good guide to the Li status of the soil.²⁷⁹ There are considerable differences in the tolerance of various plant species to Li concentrations, as well as in the plants' ability to take up this element. Borovik-Romanova and Bielova⁹² calculated the index of the biological concentrations, based on the ratio of Li in plant ash to Li in topsoil. For plants of the *Rosaceae* family with the highest mean Li content (Table 6.3), this index is 0.6; while for plants of the *Polygonaceae*, it is 0.04. The highest value of this index, 0.8, however, was calculated for plants of the *Solanaceae*, members of which are known to have the highest tolerance to Li. Some plants of this family when grown in an arid climatic zone accumulate more than 1000 mg/kg Li.⁷²⁵ The highest uptake of Li was reported for plant species growing on "Natric" soils or other soils having increased contents of alkali metals.

Lithium appears to share the K⁺ transport carrier and therefore is easily transported in plants, being located mainly in leaf tissues. The Li contents of edible plant parts show that some leaves accumulated a higher proportion of Li than did storage roots or bulbs (Table 6.4). However, a higher

TABLE 6.3
Lithium Content of Plant Families (mg/kg)

Family	Russia (Mean) (92)	United States (Range) (29, 725, 94)	New Zealand (Range) (864)
Rosaceae	2.9	—	—
Ranunculaceae	2.0	—	—
Solanaceae	1.9	0.01–31 (1120)	—
Violaceae	1.3	—	—
Leguminosae	0.67	0.01–3.1	<0.03–143
Compositae	0.55	—	—
Cruciferae	0.54	—	—
Chenopodiaceae	0.32	—	—
Urticaceae	0.24	—	—
Gramineae	0.24	0.07–1.5	<0.02–13
Polygonaceae	0.10	—	—
Lichenes	—	0.02–0.3 ^a	—

Note: References are given within parentheses.

^a Worldwide data.

TABLE 6.4
Lithium Content of Plant Foodstuffs

Plant	Tissue Sample	Mean Content (mg/kg)	
		DW Basis	AW Basis
Celery	Leaves	6.6	—
Chard	Leaves	6.2	—
Corn	Ears and stover	0.8	—
Corn	Grains	0.05	—
Cabbage	Leaves	0.5	4.9
Carrot	Roots	0.2	2.3
Lettuce	Leaves	0.3	2.0
Onion	Bulbs	0.06	1.6
Potato	Tubers	—	<4
Tomato	Fruits	—	<4
Apple	Fruits	—	<4
Orange	Fruits	0.2	5.3

Source: Data compiled from Chapman, H. D., ed., *Diagnostic Criteria for Plants and Soils*, University of California, Riverside, 793, 1972; Duke, J. A., *Econ. Bot.*, 23, 344, 1970; Shacklette, H. T., *U.S. Geol. Surv. Prof. Pap.*, 1178, 149, 1980.

Li content is very often reported for roots. The ratio of root to top for Li in ryegrass was 4.4, while for white clover it was 20.⁸⁶⁴ This may suggest that a difference in plant tolerance to Li concentration is related mainly to mechanisms of biological barriers in root tissues. Li is concentrated rather in above-earth parts of plants. This is especially noticeable in plants growing in industrial regions; for example, the leaves:roots ratio for Li in dandelion from a rural region is 0.8, and from an industrial region it is 5.0.¹³⁵¹

Wallace et al.^{844a} reported that in most experimental treatments bush beans accumulated more Li in shoots than in roots while growing in a solution culture with high concentrations of Li. They reported also that higher levels of Li decreased the Zn content in leaves and increased Ca, Fe, and Mn content in all plant tissues.

Although Li is not known to be an essential plant nutrient, there is some evidence that Li can affect plant growth and development.²⁹ However, stimulating effects of several Li salts reported by various authors have never been confirmed. This observed stimulation may also be related to the influence of other factors, including secondary effects of anions associated with Li. There have been reported antagonistic effects from Rb and possible Zn, whereas synergistic effects from Fe and Mn. Ca inhibits Li uptake by plants, thus the addition of lime to high-Li soil may reduce toxic effects of this element. Although Li is not known yet as an essential plant nutrient, there are some evidences that Li can affect plant growth and may play some metabolic function in halophytes.

Increased Li contents in soil can be toxic to some plants. Citrus trees are probably the most susceptible to an excess of Li, and their growth in salt-enriched soils can be significantly reduced due to high Li contents. In high-Li soils, damage to root tips, injured root growth, and chlorotic and necrotic spots on leaves have been observed for corn. Resistant to a high concentration of Li are plants of the *Solanaceae* family which may accumulate, when grown in “Natric” soils, even above 1000 mg/kg. Threshold concentrations of Li in plants are variable, and, for example, moderate to severe toxic effects of 4 to 40 mg Li/kg in citrus leaves were reported. Although several microorganisms are relatively sensitive to increased level of Li, some fungi *Pencillium* and *Aspergillus* are known to adapt easily to such growth media.

Lithium concentrations in moss (*Hylocomium splendens*) growing in Norway in the period 1990–1955 ranged from 0.0027 to 2.6 mg/kg (average 0.22) and have not changed as compared with Li contents in moss collected earlier (Berg and Steinnes¹²²³).

III RUBIDIUM

A INTRODUCTION

Worldwide mean values for Rb in soils vary between 18 and 116 mg/kg (Table 3.2). The upper continental crust contains Rb at around 100 mg/kg (Table 6.2). Rb behaves similarly to Li in the lithosphere and thus it is likely to be concentrated rather in acidic igneous rocks and sedimentary argillaceous rocks. Although Rb is closely linked with K, its bonding forces to silicates are stronger than those of K, and therefore K:Rb ratio continually decreases during soil-forming processes.

Rubidium is considered to be a dispersed element and does not form minerals of its own. It is associated mainly with some feldspars (e.g., pollucite) and micas (i.e., lepidolite). Micas seem to be most important Rb carriers, and contain up to 0.1% of this element.

Average global Rb content in coal is reported at 25 mg/kg (Finkelman, 1999).

World mining of Rb was estimated for <1 t in 1988, and its capacity of production in 1997 was established as 5 t. (USGS, 2004).

Rubidium is highly reactive and may ignite spontaneously in air. It is used in electronics, (production of semiconductors and photocells) and in some glass production.

B SOILS

The behavior of Rb in sedimentary and pedogenic processes is controlled mainly by the adsorption on clay minerals. Due to a relatively small diameter of hydrated ion (Table 6.1), Rb is likely to be active in soil processes. Rb reveals stronger bonding forces than K and thus it is likely to decrease the rate and activations energy of K release from micaceous minerals.⁹⁹⁹

Rubidium content in soils is largely inherited from the parent rocks, as is indicated by the highest mean Rb content, 100–120 mg/kg, in soils over granites and gneisses. Also soils of heavy texture contain relatively high amounts of Rb (Table 6.2) what is an effect of easy adsorption on clay minerals, and especially on micaceous clays. A significant positive correlation between the Rb contents and clay fraction in loess deposit was established (Waganov and Nizharadze¹¹⁸¹). The lowest concentrations of Rb, 30–50 mg/kg, are in sandy and organic soils, 1–10 mg/kg (Markert and Lieth¹⁰⁸⁶). Relatively high Rb contents were reported for soils in the United States, for which mean values ranged from 30 to 120 mg/kg, being the lowest for organic light soils and the highest for soils developed from granites and gneisses (Table 6.5).

Japanese soils contain Rb within the range from 63 to 100 mg/kg, being the lowest in Andosols and the highest in Gleysols (Takeda et al., 2004). Swedish arable soils contain Rb in the range 70–190 mg/kg, at average value of 116 mg/kg (Eriksson, 2001). The mean Rb content in light loamy soils of Poland was established as 66 mg/kg (Dobrowolski¹⁸¹) whereas for deep loess deposits in Russia it was given as 96 mg/kg (Waganov and Nizharadze¹¹⁸¹). Naidenov and Travesi⁵⁵⁸ reported Rb in Bulgarian soils to be within the range of 63–420 mg/kg (mean 179). Data presented by Govindaraju¹³¹³ for Rb in reference soil samples give a bit higher Rb contents in soils, within the range from 69 to 1141 mg/kg in soils from the United States and from 15 to 140 mg/kg for soils from China.

The content of Rb in manure is very low, and established as 0.06 mg/kg, whereas phosphate fertilizers contain at an average value of 5 mg/kg, and sewage sludges—up to about 100 mg/kg.

C PLANTS

Rubidium, as other monovalent cations, is easily taken up by plants, as are other monovalent cations. It may partly substitute for K sites in plants, as their properties are similar, but cannot substitute for

TABLE 6.5
Rubidium Content of Surface Soils of the United States (mg/kg)

Soil	Range	Mean
Sandy soils and lithosols on sandstones	<20–120	50
Light loamy soils	30–100	60
Loess and soils on silt deposits	45–100	75
Clay and clay-loamy soils	45–120	80
Alluvial soils	55–140	100
Soils over granites and gneisses	<20–210	120
Soils over volcanic rocks	20–115	65
Soils over limestones and calcareous rocks	50–100	75
Soils on glacial till and drift	30–80	65
Light desert soils	70–120	95
Silty prairie soils	50–100	65
Chernozems and dark prairie soils	55–115	80
Organic light soils	<20–70	30
Forest soils	<20–120	55

Source: Data from Shacklette, H. T. and Boerngen, J. G., *U.S. Geol. Surv. Prof. Pap.*, 1270, 105, 1984.

K metabolic roles, therefore, in high concentrations, it is rather toxic to plants. If some plants (e.g., sugar beets) are deficient in K, Rb together with Na can stimulate the growth.²¹¹ High Rb contents in plants might be toxic. Symptoms of its toxicity are dark green leaves, wilting and stunted foliage, and short brown roots, however, in field conditions they are practically unknown.

Despite the chemical similarity of Rb to K, its uptake and transportation within plants were reported to be different from those of K.^{749,839} Tyler¹¹⁷⁰ described increased availability of Rb to a wide range of vascular plants and fungi, with soil acidity, while the absorption of K is rather limited. Thus, effects of interactions between Rb and K on their availability to plants need more basic information.

The Rb contents of plants differ for each species and for parts of plants (Table 6.6). Increased levels of Rb are reported for plants from industrial regions (Kośla et al., 2001). Rühling et al.¹¹³⁵ found Rb to range from 14 to 37 mg/kg in mosses from the Nordic countries. Zajic⁸⁹⁸ reported concentrations of Rb in fungi to vary from 3 to 150 mg/kg. Some bacteria are known to accumulate Rb, as other monovalent cations, in subcellular vesicles.⁸⁵⁶ Horowitz et al.³²⁵ found the highest Rb content to be more than 100 mg/kg in some fungi. However, most of the higher plant species analyzed by these authors contained Rb in the range of 20–70 mg/kg.

IV CESIUM

A INTRODUCTION

Cesium is a relatively rare element of the naturally occurring alkali metals in the terrestrial environments. It has lithophilic properties and behaves similarly to Rb, but appears to have a greater affinity to aluminosilicates. Thus, is concentrated mainly in acidic igneous rocks and in argillaceous sediments where its contents range from 2 to 10 mg/kg (Table 6.2).

Cesium is a component of three minerals, of which only pollucite, $\text{H}_4\text{Cs}_4\text{Si}_6\text{O}_{27}$, containing Cs_2O between 5% and 32%, is of commercial importance. Most Cs, however, is dispersed in some common minerals, like micas and feldspars.

TABLE 6.6
Rubidium Content of Plant Foodstuffs and Fodders (mg/kg)

Plant	Tissue Samples	Mean Content
Cereal	Grains	4
Corn	Grains	3
Onion	Bulbs	1
Lettuce	Leaves	14
Cabbage	Leaves	12
Bean	Pods	51
Soybean	Seeds	220
Apple	Fruits	50
Avocado	Fruits	20
Clover	Tops	44
Lucerne (alfalfa)	Tops	98
Grass	Tops	130

Source: Data from Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 300, 1979 (Po); Ozoliniya, G. R. and Kiunke, L. M., *Fizyologo-Biokhimicheskiye Issledovaniya Rasteniy*, Zinante, Riga, 111, 1978 (Ru); Shacklette, H. T., Erdman, J. A., and Harms, T. F., *Toxicity of Heavy Metals in the Environments, Part I*, Marcel Dekker, New York, 25, 1978.

Annual global production of Cs is estimated as 5.9 Mt (USGS, 2004). It is used in production of vacuum tubes, rockets propellant, some photo cells, and accurate atomic clocks. Some Cs compounds are also used as catalysts in organic synthesis.

Mean Cs content in coal is about 1 mg/kg (Finkelman, 1999).

Radioactive ^{137}Cs has been approved for the sterilization of some foods, surgical equipments, and so on.

B SOILS

Cesium released by weathering is strongly adsorbed in soils. Studies with radiocesium indicated an increased concentration of Cs in fine granulometric soil fraction (Paasikallio, 1999). A great capacity to bind this metal by micaceous minerals (e.g., illites) is reported by Hinton et al. (2006) and Nakao et al. (2003).

The mean background Cs contents for worldwide soils range from 1.7 to 8.0 mg/kg (Table 3.2). Average contents in soil groups range between 5 and 10 mg/kg (Table 6.2). Wedepohl⁸⁵⁵ calculated the range of Cs in soils as 0.3–26 mg/kg. Agricultural soils in Japan contain Cs at the range 1–11 mg/kg, whereas pine forest litter contain from 0.29 to 0.98 mg/kg (Tsukada et al., 1998, 2002). Swedish arable soils has Cs in the range from 0.3 to 4.5 mg/kg (Eriksson, 2001). Koons and Helmke⁴⁰⁹ gave the range to be from 0.3 to 5.1 mg/kg Cs in four Canadian reference soils, and Naidenov and Travesi⁵⁵⁸ found Cs levels in Bulgarian soils to range from 2.2 to 16.7 mg/kg, being the highest in surface forest soil and chernozems. Waganov and Nizharadze¹¹⁸¹ reported the Cs mean content of deep loess deposit in the European part of Russia to be 3.2 mg/kg. Markert and Lieth¹⁰⁸⁶ found Cs in peat bogs in Germany and in Sweden to be within the range 0.1–1 mg/kg. Govindaraju¹³¹³ reported that the Cs contents in reference soils from China range from 2.7 to 21.4 mg/kg (mean 9.31), and in soils from the United States, from 0.41 to 5.07 mg/kg (mean 3.03).

C PLANTS

Cesium is not essential to plants and thus its distribution in plant samples has not been studied intensively. This element is relative active in soils and easily taken up by plants, especially from sandy acid soils. Cs distribution in plants is similar to K which suggests that this metal can compete with K uptake and K binding sites in cells (Isaure et al., 2006). Thus, Cs phytotoxicity might be due to these interactions. An addition of lime and peat to soil greatly inhibited the phytoavailability of this metal. Fritsch et al. (2008) investigated an influence of earthworms on soil-to-plant and soil-to-snail transfer of radiocesium, and observed that only the second chain transfer was significantly increased at a presence of earthworms.

On the basis of a few compiled data, Cs common range in various plants can be presented as <0.1–3 mg/kg. Usually lower contents of Cs are in top of plants. Roots of higher plants contain about twice as much Cs (0.32 mg/kg) as old leaves (0.16 mg/kg). Young leaves contain much smaller amount of Cs –0.07 mg/kg (Ozoliniya and Kiunke⁵⁸⁸). Tsukada et al. (2002) observed increasing Cs levels from below 0.01–0.02 mg/kg in older leaves of rice. According to Tsukada and Hasewaga (2002), up to 77% of Cs was accumulated in nonedible leaves of cabbage. A very broad range of Cs (0.005–1.6 mg/kg) was noticed for mushrooms sampled from a forest in Japan (Tsukada et al., 1998).

Aidinian⁷ found 0.5–1 mg/kg Cs in tea leaves (AW), and Inarida et al.¹⁰³² found Cs in different kinds of tea leaves to be widely variable, from 0.01 to 0.31 mg/kg, with the highest averages in jasmine tea of China and in black tea of India.

Rühling et al.¹¹³⁵ found Cs to range from 0.3 to 0.48 mg/kg in mosses samples from Nordic countries in 1985. Mosses collected in Norway in the period 1990–1995 had mean Cs content 0.26 mg/kg, within the range 0.019–3.1 mg/kg (Berg and Steinnes¹²²³).

D CESIUM ISOTOPES

Radioactive isotopes, ^{134}Cs and ^{137}Cs , are produced by nuclear fission in nuclear power plants and occur also in fallout from nuclear weapons. Environmental concern with radiocesium in soils and food chain is largely a consequence of two events: (1) worldwide fallout from above ground nuclear weapon testing, and (2) release during the Chernobyl disaster (1986).

One of many Cs isotopes, ^{137}Cs is of special concern because it is a by-product of atomic energy production and nuclear weapons testing. Anthropogenic sources of this radionuclide also include the mining and processing of pollucite ore. Ash from coal burning and municipal waste incinerations may be a source of ^{137}Cs .

The fate of ^{137}Cs was widely studied after the fallout following the Chernobyl accident. At this accident ^{134}Cs was also released, but this radionuclide is of a much less concern because it was released in a significantly smaller quantity and has a relatively short half-life ($t_{1/2}$ is 2.1 years) compared with ^{137}Cs ($t_{1/2}$ is 30.2 years). The deposition of both radionuclides was not only in the zone surrounding the reactor, but also in several European countries, as well as on other continents.

Soils. The geochemical characteristics of the long-lived ^{137}Cs (half-life around 30 years) are fairly similar to those of the stable Cs. Thus, when it is deposited on soils it becomes strongly adsorbed by clay fractions, clay minerals, and OM, and thus migrates quite slowly in soil (Tsukada et al., 2008). Zacccone et al. (2007) observed that highly organic soils, and ombrotrophic bogs in particular, show a radiocesium peak corresponding to the Chernobyl accident. Especially SOM of higher molecular weight, is likely to accumulate a large proportion of the ^{137}Cs and therefore influences its relatively low mobility (Agapkina et al., 1995). Also Fe and Mn sesquioxides decrease the mobility, and thus the migration rate of this nuclide (Arapis et al., 1997; Grin et al.¹³¹⁷). In fresh alluvial sediments, most of the Cs was held by either amorphous Fe-oxyhydroxides or OM (Kaplan et al., 2005). In general, clay fraction contributes to the immobilization of ^{137}Cs ,

however, at the presence of hydromica its increased mobilization is observed (Korobova and Chizhikova, 2006).

Horizontal distribution of Cs radionuclides in soils seems to be correlated with seasonal microbiota activity (Kostyuk and Bunnenberg¹³⁷⁰). Results of investigations about a decade after the Chernobyl accident indicated that up to 90% of the inventory of radiocesium was still contained in the top 3–7 cm soil layer and ranged from 103 to 1500 kBq/m² (Kagan and Kadatsky, 1996). Schimmack et al.¹¹⁴⁰ reported that the rates of vertical migration of ¹³⁴Cs and ¹³⁷Cs deposited on grassland soil by fallout from the reactor accident in Chernobyl was considerably faster (0.2 and 0.3 cm/h) than of those from the long-term migration of ¹³⁷Cs from the global fallout of weapon-testing.

Reported concentrations of ¹³⁷Cs in other soils vary from 1.7 to 28.2 Bq/kg in paddy field soils, and from 1 to 37 Bq/kg in agricultural soils of Japan (Tagami and Ushida¹⁵¹², Tsukada and Nakamura, 1999). Soils of Louisiana were reported to contain ¹³⁷Cs at the surface within the range from 1 to 92 Bq/kg (Meriwether^{1090a}) and soils of the wetland in South Carolina contain this radionuclide in the range of 0.2–10.1 Bq/g, with the highest values for moisture-regime location (Kaplan et al., 2005). Surface soils in the Tatra Mountain area, Poland, contained this radionuclide within the range of 160–650 Bq/kg.¹³¹⁴ In Russia (Bryansk region) soils, after the Chernobyl accident, accumulated ¹³⁷Cs was within the range of 703–899 Bq/m², mainly in the surface layer. Its fraction insoluble in water varied from 40% to 93% of the total content (Korobova et al., 1998). Soils of Kazakhstan sampled in 1992 contained ¹³⁷Cs in the range of average values from 82 to 120 mCi/km² (Panin, 2004). According to Zhiyanski et al. (2006) higher ¹³⁷Cs contamination was noticed in soils of the central region of Bulgaria (0.92–21.2 kBq/m²) than in the mountain region (0.92–7.1 kBq/m²).

Soil samples collected during 1999–2001 in France had the activity of ¹³⁷Cs above 10 kBq/m² in the surface layer (Renaud et al., 2003). These authors demonstrated a close relationship between ¹³⁷Cs deposition and the rainfall of the first week of May 1986, right after the Chernobyl accident. The impact of industrial pollution on the levels of ¹³⁷Cs has been reported by Outola et al. (2003) for forest soils surrounding the Cu–Ni smelter in Finland. Soil samples taken in 2000 had the total deposition of ¹³⁷Cs in the range 15–25 kBq/m² being the highest at the distance of 2 km from the smelter.

The fate of ¹³⁷Cs in various soils, 5 years after the fallout following the Chernobyl accident, was investigated by Mondini et al.¹⁴²⁴ The distribution of this radionuclide was related to OM content (highly concentrated in the top organic soil layer) and to the CEC. Its content was higher in calcareous soils than in soils derived from siliceous parent material. The highest concentrations of the radionuclide, which ranged from 841 to 1622 Bq/kg, were in litter layers. In Scotland, up to 50% of ¹³⁷Cs emitted during the Chernobyl accident remains in the surface soil layer.¹³³¹

Median values for the inventory of ¹³⁷Cs in topsoils of Belarus, about a decade after the Chernobyl accident, ranged from 103 to 1500 kBq/m², and the highest concentration was as much as 600 times higher than the preaccident value.¹³⁶⁰ The authors estimated that about 90% of the inventory of ¹³⁷Cs is contained in the top 3–7 cm soil layer. Results of recent studies on the mobility of ¹³⁷Cs issued from the Chernobyl accident indicate that the presence of increased content of clay minerals in soils, Fe and Mn sesquioxides and OM decrease the mobility, and thus the migration rate of this nuclide.¹³¹⁷

The role of microbiota in the behavior of radionuclides has been extensively studied.¹³⁷⁰ Horizontal distribution of radionuclide deposits and temporal pattern of radio contamination are directly correlated with the seasonal microbiota activity. Also, climatic factors are of great importance in governing the behavior of radionuclides in the environment; however, more studies in this field are needed.¹²⁴⁹

Plants. Radioactive Cs, similarly to the stable Cs, is easily absorbed by higher plants and microorganisms. Plants take up more ¹³⁷Cs from light sandy soils than from loamy soils and soils rich in organic matter (Table 6.7). Paasikallio (1999) reported that the most effective agent for the

TABLE 6.7
Concentrations of ^{137}Cs (nCi/g) in Various Plants Grown on Soils with the Addition of 0.03 nCi/kg

Plant and Part	Sandy Soil		Loamy Soil		Chernozem	
	FW	DW	FW	DW	FW	DW
Cabbage, leaves	4.0	34.9	0.4	6.3	0.6	8.3
Carrot, roots	0.9	6.5	—	—	0.2	1.5
Beet, roots	1.0	5.1	0.4	2.2	0.3	1.6
Potato, tubers	1.3	5.9	1.0	2.3	0.6	2.3
Cucumber, fruits	0.3	8.1	0.1	2.5	0.1	2.4
Tomato, fruits	0.11	2.5	0.02	0.6	0.03	1.2
Oat, straw	—	10–19	—	—	—	—
Oat, grain	—	3–15	—	—	—	—

Source: Data from Guliakin, I. V., Yudintseva, E. V., and Gorina, L. J., *Agrokhimiya*, 7, 121, 1975a (Ru); Guliakin, I. V., Yudintseva, E. V., and Levina, E. M., *Agrokhimiya*, 2, 102, 1976 (Ru).

reduction in the uptake of ^{134}Cs , especially in the long-term, was biotite and a biotite–zeolite mixture.

White et al. (2003) stated that the specific mechanism by which Cs is taken up by root cells can be adapted to develop plant species for the phytoextraction of radiocesium from soils. Some plants, such as *Amaranthus* and *Helianthus* species, exhibit a relatively great accumulation of this radionuclide and are suggested for the phytoremediation of polluted sites (Dushenkov and Sorochinsky¹²⁸³). The increased accumulation of ^{137}Cs in the roots of *Epipremnum* plants is proposed as a method of rhizofiltration of this radionuclide (Kamel et al., 2007).

Grogan et al.¹⁰¹⁶ studied soil–plant transfer factors for several radionuclides and found that ^{137}Cs is relatively easily taken up by winter wheat. Some grasses can accumulate up to 36% of the total amount of ^{137}Cs from the growth media after the first five harvests, and the concentrations of this radionuclide in grass correlates curvilinearly with its content of the growth media.¹²⁹² Jegadeeswari et al. (2005) reported a much higher accumulation of radiocesium by sorghum roots (mean activity 696 Bq/pot) than by whole plant (mean 8.52 Bq/pot). Radioactive Cs is more easily taken up by rice than the stable Cs, apparently due to a higher biological activity (Tsukada and Nakamura, 1999). Mycorrhiza of heather roots acts as a barrier and limits the transfer of this radionuclide from roots to tops¹³³¹.

Plant uptake of ^{137}Cs has been studied because of concern about radioactive emissions from nuclear tests and stations, especially after the Chernobyl disaster. A willow grown on a ^{134}Cs artificially contaminated site took up only a small fraction of this nuclide since most of ^{134}Cs was returned in autumn by litter fall or leached by rainwater.¹³¹¹ On the other hand, *Amaranthus* and *Helianthus* species are reported to accumulate a significant amount of ^{137}Cs and are suggested as an alternative for the phytoremediation of polluted sites.¹²⁸³ As reported by Tsukada et al.,¹⁵²² this radionuclide is more easily taken up by rice than the stable Cs, apparently due to a higher biological activity of this radionuclide compared to Cs.

Increased levels of ^{137}Cs in mosses (up to 1140 Bq/kg) from Syrian coastal mountains indicate its atmospheric origin (Al-Masri et al., 2005). Radioactive Cs in lichens sampled from 1986 to 1988 from the Tatra Mountains National Park in Poland was at similar levels, ranging from 1510 to 8120 Bq/kg, and was about tenfold higher than that measured in 1985 (range 480–790 Bq/kg).¹³¹⁴ Recent studies in a Lithuanian forest indicated that during the period from 1986 to 1992, the radioactivity in lichens due to ^{137}Cs and ^{134}Cs decreased by a factor of two to three orders (10–100 times).¹²⁸¹

The highest accumulation of radiocesium is in mushroom pericarp, and therefore the health-related limit for ^{137}Cs in edible mushrooms is established in Europe at 600 Bq/kg.¹³⁵⁷ The median content of radiocesium in 110 samples of mushrooms (65 species) collected in 1990 in Japan was (in Bq/kg) 60 for ^{137}Cs , and <7 for ^{134}Cs . Soil–mushroom transfer factors were in the range 5.5–13.¹⁵⁶³ Mushrooms reveal a great ability to accumulate radiocesium what might be its source in food products (Yordanova et al., 2007).

7 Elements of Group 2 (Previously Group IIa)

The trace elements of Group 2, beryllium (Be), strontium (Sr), and barium (Ba), belong to the alkaline earths and behave similarly to Ca and Mg. Their physical properties, especially sizes of their ionic radii are fairly similar to those of Ca, and they may substitute for each other, however, the small ionic radius of Be prevents its replacement by other cations (Table 7.1). A characteristic of these cations is the small ionic radius and high charge to radius ratio. All the alkaline earths are associated with the carbon cycle that strongly controls their behavior in the environment. Be in the terrestrial environment is more susceptible to hydrolysis and complexation processes than other elements of this group.

Radionuclides of this group, and especially ^{90}Sr and ^{226}Ra , could present significant risk of environmental hazard. Radium (Ra), which occurs as several radionuclides, is a product after the decay chain of U and Th.

I BERYLLIUM

A INTRODUCTION

The abundance of Be in the Earth's upper crust averages 3 mg/kg, but the range of 4–6 mg/kg has been cited quite frequently (Figure 3.2). Be is the lightest of the alkaline earths and although widely distributed, exists in relatively small quantities and is likely to concentrate in acid igneous rocks and in argillaceous sediments, where its contents reach up to 6 mg/kg, (Table 7.2). However, some alkaline rocks tend to be enriched in this element.

Organic matter reveal a sorption capacity for Be, and thus its concentrations in coal vary broadly from 11 to 330 mg/kg and average 2.5 mg/kg (Finkelman, 1999; Llorens et al., 2000). However, higher contents of Be, from 100 to 1000 mg/kg, have also been reported, and the highest Be concentration, up to 2000 mg/kg, was found in coals from the North Bohemian Basin in the Czech Republic (Vesely et al., 2002). Crude oil may content from 0.0005 to 0.5 mg Be/kg, depending upon local geochemical conditions.

Beryllium reveals lithophilic affinity; it is similar to Al in geochemical behavior and can substitute for Si and Al in some minerals, and it can strongly bond, especially to montmorillonitic clays. Over 100 naturally occurring minerals contain essential amounts of Be. The most common its own mineral is beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, associated mainly with pegmatite bodies, where crystals of beryl may comprise a few percent of the total volume. Other minerals like bertrandite, $\text{Be}_4\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$; bromeline, BeO ; and chrysoberyl, BeAl_2O_3 ; are relatively rare. Of these minerals, beryl and bertrandite are of commercial importance.

Beryllium occurs in several isotope species (8), of which only ^9Be is stable, and ^7Be and ^{10}Be are both cosmogenic and produced by nuclear reaction induced by cosmic rays or accelerator mass spectrometry.

Global Be mining is calculated as 2.55 kt in 2003 (WMSY, 2004). Be oxide is the most important commercial product and the Cu–Be alloy is the most commonly used in metallurgy. Together with the use in electronic and electrical components (i.e., electrical insulators, submarine cables), these applications accounted for more than 80% of its consumption. It is also used in several precision

TABLE 7.1
Selected Properties of Trace Elements of Group 2

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C) (g/cm ³)	Valence
Be, beryllium	4	9.01	140	1.85	+2
Sr, strontium	38	87.63	245	2.46	+2
Ba, barium	56	137.33	278	3.5	+2
Ra, radium	88	226.03	—	5.0	+2

^a Approximately average values.

instruments for aircraft/satellite structures, rocket propellants, atomic reactors, high-speed computers, high technology ceramics, as well as in other special facilities.

B SOILS

The mean Be background contents of worldwide soils range from 0.92 to 2.0 mg/kg (Table 3.2). Geometric means for Be in various soils of Poland are 0.33 and 0.73 mg/kg, for light sandy and heavy loamy soils, respectively (Kabata-Pendias and Mukherjee, 2007). In Japanese soils it varies from 0.5 mg/kg in Andosols to 1.5 mg/kg in Gleysols (Takeda et al., 2004). Swedish arable soils contain Be in the range from <0.5 to 1.8 mg/kg, at an average value of 1.3 mg/kg (Eriksson, 2001). Average Be contents in Florida and California soils are given as 0.46 and 1.14 mg/kg, respectively, and mean content in the U.S. soils is estimated at 0.6 mg/kg (ATSDR, 2002).

Bourtles¹²⁴⁰ described that both radionuclides exhibit a great affinity for either inorganic or organic particles of soil and ¹⁰Be is especially likely to be concentrated in organic-rich sediments and soils.

Most of recent data for soil Be are related to contaminated soils. Due to some new technologies and uses of Be, as well as to coal combustion, there is concern that Be may be increasing in

TABLE 7.2
Abundance of Trace Elements of Group 2 in Rocks and Soils (mg/kg)

Rock/Soil	Be	Sr	Ba
Earth's crust	4–6	260–370	250–584
Igneous rocks			
Mafic	0.3–1.0	140–460	250–400
Acid	3–6.5	60–400	400–1200
Sedimentary rocks			
Argillaceous	2–6	300–450	500–800
Sandstones	0.2–1.0	20–140	100–320
Calcareous	0.2–2.0	460–600	50–200
Soils ^a	1.9	147	362
Arenosols (sandy)	0.1–1.7	5–1000	85–780
Podzols (medium loamy)	0.73–1.8	20–1000	200–1500
Cambisols (heavy loamy)	2.5–4.9	20–3100	200–1500
Calcisols (calcareous)	2.5	5–1000	150–1500
Histosols (organic)	—	70–500	10–700

^a Soil groups are given according to the WBR (Table 3.1).

agricultural soils. Considerable Be concentrations were reported for some soils in Alaska, up to 300 mg/kg, and for soils over Be-rich granite in Czech Republic, up to 15 mg/kg (Veselý et al., 2002). The degree of soil pollution in this region reflects the isolines of fly ash deposition, as an effect of the increased Be content in coal. Soils from the San Joaquin Valley of central California, described as “uncontaminated” and “highly contaminated” contain Be at mean levels, 2.0 and 3.2 mg/kg, respectively (Wilson et al., 1994). Concentrations of Be in the range 0.46–4.7 mg/kg are in soils at the Nevada Nuclear Weapons Test Site (Patton *vide* Veselý et al., 2002). High Be contents, up to 55 mg/kg, was reported for soils in the neighborhood of the Be factories in Japan (Asami⁹²⁵).

Beryllium occurs most often as divalent cation (Table 7.1), and its complex ions also are mainly divalent: $(\text{BeO}_3)^{2-}$, $(\text{Be}_2\text{O}_3)^{2-}$, and $(\text{Be}_2\text{O})^{2+}$. Common anionic complexes in alkaline environments are $\text{Be}(\text{OH})\text{CO}_3^-$, and $\text{Be}(\text{CO}_3)_2^{2-}$. Although Be appears to be rather immobile in soils, its salts, such as BeCl_2 and BeSO_4 , are easily soluble and available, and therefore potentially toxic to plants. Its concentration in solutions of various soils ranges from 0.2 to 1.1 $\mu\text{g/L}$, mainly as simple cations, Be^{2+} and BeOH^+ , and anions, BeO_3^{2-} and $\text{Be}(\text{OH})_3^-$ (Kabata-Pendias and Sadurski, 2004). As reported by Krám et al.,¹³⁷⁶ Be is especially highly mobile under the condition of acidic (pH 3.4) forest soil, which can have serious environmental consequences in temperate climate regions. Most Be in soil does not dissolve easily in soil solution and remains in bound forms; its binding increases with increasing pH. Also SOM (mainly FA) reveal a greater sorption capacity for Be with increasing pH. There is observed a decrease of Be mobility with dissolved Al and dissolved organic carbon concentration (Veselý et al., 2002). A close positive relationship was reported for Be and clay fraction contents in soils, and it is likely to be more strongly bound by clay minerals than by organic matter (Kabata-Pendias and Mukherjee, 2007).

Beryllium is easily accumulated in organic soil horizons and is strongly bound layers enriched in montmorillonitic clays. Although Be appears to be rather immobile in soils, its readily soluble salts, such as BeCl_2 and BeSO_4 , can be available and therefore toxic to plants. The distribution of Be in the soil profiles also reflects the leaching processes of the element and shows its accumulation in the subsoil layers. The concentration of Be in soil solutions varies from 0.21 mg/L in surface soil layer to 1.1 mg/L in mother material (leucogranite). Hädrich et al.²⁹⁸ reported the range in Be concentrations in soil solutions as 0.4–1.0 mg/L.

As Bourles¹²⁴⁰ described both radionuclides reveal a great affinity for either inorganic or organic particles of soil. ^{10}Be is especially likely to be concentrated in organic-rich soil.

C PLANTS

Mechanisms of the Be absorption by plants seem to be similar to those involved in the uptake of major divalent cations, Mg^{2+} and Ca^{2+} . However, these elements reveal antagonistic interactions, and Be is known to substitute for Mg, especially in some plants. Plants can easily take up Be when it occurs in mobile forms in soils.

Mean contents of Be in plants vary broadly from 0.001 to 59 $\mu\text{g/kg}$ FW (Table 7.3). Some plants of the *Leguminosae* and *Cruciferae* families reveal a great ability to accumulate Be, particularly in their root tissues. In some plant shoots increased levels of Be have been observed, for example, lettuce leaves—33 $\mu\text{g/kg}$, and tomato fruits—240 $\mu\text{g/kg}$ (Krampitz⁴²⁵). Vaessen and Szteke¹⁵²³ reviewed Be contents in food plants of several countries and gave range of mean values for Be from 0.07 to <25 $\mu\text{g/kg}$ FW, with the lowest for beans, and the highest for corn (Table 7.3).

Increased levels of Be in plants, over that of baseline concentrations, can be a good indicator of pollution, mainly from industrial sources (Sarosiek et al.¹⁴⁷⁷). Be in tissues of trees grown in the polluted region of Bohemia in the Czech Republic showed the highest concentrations in spruce needles (310 $\mu\text{g/kg}$) and in beech leaves (230 $\mu\text{g/kg}$), while its contents in stem wood and bark varied within the range 3–78 $\mu\text{g/kg}$ (Skřivan et al. *vide* Veselý et al., 2002). Moss samples from Norway, collected in the period 1990–1995 contained Be within a very broad range, from <0.4 to 370 $\mu\text{g/kg}$ (Berg and Steinnes¹²²³).

TABLE 7.3
Beryllium in Food Plants^a (µg/kg FW)

Plant	Range	Mean
Cereal grain	—	<0.5
Beans	<0.001–0.07	0.07
Cabbage	—	0.2
Green pepper	—	42
Lettuce	—	16
Carrots ^b	<25	—
Corn, field ^b	—	<25
Potatoes, tubers	0.4–59	—
Rice	3–5	4
Tomato	0.2–17	240 ^d
Mushrooms ^c	<3–36	9

DL—Detection limits.

^a Adapted from Vaessen, H. A. M. G. and Szeke, B., *Food Addit. Contam.*, 17, 149, 2000. Unless otherwise indicated.

^b After ATSDR 2002. *Draft Toxicological Profile for Several Trace Elements*. U.S. Dept. Health & Human Services. Agency for Toxic Substances and Disease Registry, Atlanta, GA.

^c European wild.

^d The highest value, after Krampitz, G., Die biologische Bedeutung von Beryllium-Verbindungen. In: *Proceedings of the Arsen Symposium*, Anke, M., Schneider, H. J., Brückner, Chr., eds., Friedrich-Schiller University, Jena, E. Germany, 245, 1980.

The toxicity of Be to plants has been frequently reported, and was observed at the concentration range in soils from 10 to 50 mg/kg. However, according to the results of Hlušek (2000), above 2 mg Be/kg soil affected yield decrease of lettuce, up to 40%. The Be concentration in nutrient solution ranging from 2 to 16 mg/L is highly toxic to plants, reducing root length of collard and of wheat by 50%; concentrations >8 mg Be/L totally inhibited seed germination (Gettier and Adriano¹⁰⁰⁹). Increased levels of Be in plants reduce growth, inhibit the uptake of Ca, Mg, and partly of P, and degrade some proteins and enzymes. Although specific symptoms of Be toxicity to plants are not known, the common symptoms are brown, retarded roots, and stunted foliage. Gough et al.²⁷⁹ and Krampitz⁴²⁵ reported stimulating effects of the dilute solution of Be(NO₃)₂ on the growth of several plant species, and microorganisms (*Aspergillus niger*) in particular. Biochemical mechanisms of this phenomenon, however, are not clear.

Beryllium apparently is easily taken up by plants when it occurs in soluble forms in soils. Most Be taken up by plants remains in roots and only a very small proportion of absorbed Be is translocated to above-ground plant parts.

II STRONTIUM

A INTRODUCTION

Strontium is a relatively common element in the Earth's crust and its contents range between 260 and 370 mg/kg. It is likely to concentrate in mafic igneous rocks and in calcareous sediments. Clay minerals have a large capacity to absorb Sr, and thus most argillaceous sediments are enriched in this element (Table 7.2). Both geochemical and biochemical characteristics of Sr are similar to those of Ca. Sr reveals lithophilic affinity and is associated with Ca, and in smaller extents with Mg. The

Ca to Sr ratio, in particular environments, may reflect, to a certain extent, the abundance of Sr and its biogeochemical properties. Sr occurs mainly as bivalent cation (Table 7.1), however, its chelated forms play an important role in the cycling. Most Sr is likely to precipitate as biogenic carbonates, largely in the form of invertebrate shell material.

Geological occurrence of Sr is associated mainly with calcareous rocks and sulfur deposits. The distribution of Sr in minerals is largely controlled by Ca, the ionic radius of which is fairly similar to that of Sr, thus it is likely to concentrate in calcium-rich minerals and to be incorporated in calcite and aragonite. During the formation of calcareous and sulfuric sediments, Sr is mobilized as easily soluble strontianite, SrCO_3 , and later deposited as celestite, SrSO_4 . These both minerals are commercially important minerals. Strontium occurs also in several other minerals, for example, nordite or belovite, which are in association with Na and lanthanides.

Strontium world mine production in 2000 was 320 kt (USGS, 2004). It does not have direct applications as a pure metal. However, its various compounds are broadly used (e.g., above 80% of all Sr consumed in the United States) in the manufacturing of ceramics and glass. All color televisions in the United States are required by law to contain Sr in the faceplate glass of the picture tube to block x-ray emissions (ATSDR, 2002). Other uses of Sr compounds are in various technologies of metallurgy, luminescent paint pigments, and some medicines.

B SOILS

Worldwide reported background Sr contents of soils ranges from 130 to 240 mg/kg (Table 3.2). Sr is easily mobilized during weathering, especially in oxidizing acid environments, thus is incorporated in clay minerals and strongly fixed by OM. The Sr to Ca ratio seems to be relatively stable in the biosphere and therefore is commonly used for the identification of built-up concentrations of Sr in a particular environment. A Ca to Sr ratio less than 8 indicates a possible toxicity of Sr.

Strontium content of soils is highly controlled by parent rocks and climate, its concentrations are the highest in heavy loamy soils (up to 3100 mg/kg) (Table 7.2). Geometric means (for over 4000 samples) of Sr contents in soils of Poland show a relation with textural soil groups, as follows (in mg/kg): sandy soils, 10; light loamy soils, 7; and heavy loamy soils, 24.¹³⁵⁷ However, in some calcareous soils and soils from industrial regions, Sr contents above 1000 mg/kg have been reported.¹³⁹⁰ According to Govindaraju¹³¹³ the Sr contents in reference soils from China range from 26 to 150 mg/kg, and in soils from the vicinity of a polymetallic ore field from 180 to 380 mg/kg. Sr in Venezuelan soils varies from 13 to 39 mg/kg (geometric mean values).¹²²⁷ Soils from the San Joaquin Valley of the central California contain Sr, at mean levels from 236 to 246 mg/kg (Wilson et al., 1994). Median Sr concentrations in Japanese agricultural soils range from 32 to 130 mg/kg, in Acrisols and Gleysols, respectively (Takeda et al., 2004). Swedish arable soils contain Sr in the range from 112 to 258 mg/kg, at the average value of 163 mg/kg (Eriksson, 2001).

Strontium is moderately mobile in soils, and the predominated cation, Sr^{2+} , is likely to be sorbed in hydrated form by clay minerals and Fe oxides and hydroxides. In calcareous soils, Sr may precipitate as strontianite and become less mobile. Its distribution in soil profiles follows the general trends of soil solution circulation; thus, in acid soils is likely to be leached down the profile, while in calcareous soils and in SOM rich soil layers, Sr can be concentrated in upper horizons.

Main source of Sr pollution are associated with coal combustions and sulfur mining. In organic surface layers of soils of Norway, an enrichment in Sr content as compared to C horizons is explained as an evidence of the atmospheric input of sea-salt.¹⁵⁰⁵ Displacement of Sr by Ca solutions has practical implications in the reclamation of contaminated soils.⁴⁵⁰

Strontium in phosphorites may be concentrated up to 2000 mg/kg and thus it can be also a local source of soil contamination due to phosphate fertilizers. Some soil-amendment materials containing elevated amounts of Sr might be a source of pollution. Average contents of Sr in these materials are (in mg/kg): P-fertilizers, 610; limestone, 610; manure, 80; communal sludges, 75; and industrial sludges, 270.

C PLANTS

The content of Sr in plants is highly variable (Table 7.4) and seems to be the lowest in grains (means 1.5–2.5 mg/kg) and the highest in vegetable leaves (means 45–74 mg/kg) and in tops of legume feed plants (means 219–662 mg/kg). In the European forest ecosystem, Sr in blueberries (*Vaccinium* sp.) is reported to range between 4.5–5.5 and 2.9–3.9 mg/kg, in Russia and Germany, respectively (Markert and Vtorova¹⁴⁰⁰). Although Sr seems to be not very readily transported from roots to shoots, most often its content in plant tops is relatively high, which may be an effect of aerial deposition. In most cases, however, Sr is likely to be accumulated in roots (Figure 7.1). The highest uptake of Sr is from acid light sandy soils.

Although Sr is apparently not a plant micronutrient, it is absorbed following the plant's metabolic requirements for Ca and is related to both the mechanisms of mass flow and exchange diffusion.²⁰⁹ The Ca to Sr ratio of uptake was proposed by some authors to determine the source of these cations and the rate of their uptake. Interactions between Sr and Ca are complex, and although they can compete with each other, Sr cannot replace Ca in biochemical functions. Increased level of Ca in growth media may both inhibit and stimulate Sr uptake by plants, depending on several soil and plant factors. Most often, however, addition of Ca to soil decreases Sr phytoavailability (Figure 7.1).

TABLE 7.4
Strontium in Food and Feed Plants (mg/kg)

Plant	Tissue Sample	Range	Mean
Wheat	Grains	0.48–2.3	1.5
Oats	Grains	1.8–3.2	2.5
	Green tops	9–31	20
Corn	Grains	0.06–0.4	—
Lettuce	Leaves	—	74
Spinach	Leaves	45–70	—
Cabbage	Leaves	1.2–150	45
Bean	Pods	1.5–67	18
Soybean	Leaves	58–89	—
Carrot	Roots	1.5–131	25
Onion	Bulbs	10–88	50
Potato	Tubers	—	2.6
Tomato	Fruits	0.4–91	9
Apple	Fruits	0.5–1.7	0.9 ^a
Orange	Fruits	—	0.5 ^a
Clover	Tops	95–850	219
Lucerne (alfalfa)	Tops	50–1500	662
Grass	Tops	6–37	24

Source: Data compiled from Chapman, H. D., ed., *Diagnostic Criteria for Plants and Soils*, University of California, Riverside, 793, 1972; Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 300, 1979 (Po); Mathur, S. P., Hamilton, H. A., and Preston, C. M., *Commun. Soil Sci. Plant Anal.*, 10, 1399, 1979; Oakes, T. W., Shank, K. E., Easterly, C. E., and Quintana, L. R., *Trace Subst. Environ. Health*, Vol. II, University of Missouri, Columbia, MO, 123, 1977; Shacklette, H. T., *U.S. Geol. Surv. Prof. Pap.*, 1178, 149, 1980; Wasserman, R. H., Romney, E. M., Skougstad, M. W., and Siever, R., *Geochemistry and the Environment*, Vol. 2, N.A.S., Washington, D.C., 73, 1977.

^a FW basis.

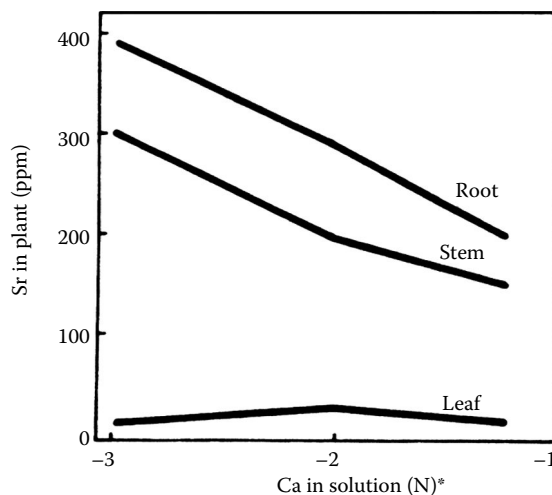


FIGURE 7.1 Effects of Ca on Sr distribution in bush beans exposed for 48 h to 10^{23} N Sr in solution culture. * Ca normality is given in powers of 10. (Based on Wallace, A. and Romney, E. M., *Agron. J.*, 3, 245, 1971.)

Weinberg⁸⁵⁶ reported that the enzyme amylase with Sr^{2+} substituted for Ca^{2+} had full activity, but varied in some physical properties. Liming of soil may have both inhibiting and stimulating effects, depending on soil and plant factors.⁴⁵⁰ However, in bush beans grown in solution culture, Ca decreased Sr content, particularly in root and stem. Reported interactions between Sr and P apparently are related to processes in soil; however, opinions vary as to the effects of P on Sr adsorption by plants.^{175, 439}

According to Takeda et al. (2005), the exchangeable Sr to Ca ratio in the soil could be a good predictor of the Sr concentration in komatsuna (*Brassica rapa*). The distribution of Sr in plants is highly variable, for example, 0.6% of the total Sr in rice plants was in polished grains and about 99% was in the nonedible parts, of which 87% was in straw (Tsukada et al., 2005). Kozhevnikova et al. (2007) observed that Sr was accumulated mainly in walls of the root cap cells. Both Sr deposited on the plant surface and taken up by roots can be easily absorbed and translocated to other parts of the plant. Soil-to-plant transfer ratios are relatively high and calculated to range 0.017–1.0 (ATSDR, 2002). Petrescu and Bilal (2006) observed that Sr taken up by conifers is accumulated mainly in roots. The authors suggested that planting conifers on uranium waste slopes may decrease the Sr migration to water systems.

Strontium in mosses sampled in Norway in the period 1990–1995 ranges from 2.8 to 51 mg/kg and averages 15 mg/kg and was somewhat lower than data reported earlier (Berg and Steinnes¹²²³). Bowen⁹⁴ gave the broad range for the Sr concentrations in lichens as 0.8–250 mg/kg.

⁹⁰Sr is easily taken up by plants, but its availability may be inhibited by the application of Ca, Mg, K, and Na to soils. Beans grown on soil treated with ⁹⁰Sr, accumulated up to 565 nCi/g in leaves, while in grains, only 24 nCi/g was accumulated.²⁹⁰ This radionuclide (in a similar experiment) ranged in oat straw from 17 to 137 nCi/g and in oat grain from 1 to 11 nCi/g.^{291,292} Alamo switchgrass can accumulate up to 44% of the total amount of ⁹⁰Sr from the growth media after the first five harvests, and the uptake of this radionuclide is correlated curvilinearly with substratum.¹²⁹² Also, *Amaranthus* species are reported to be effective in phytoextraction of this nuclide from soils in the Chernobyl exclusion zone.¹²⁸³

D STRONTIUM ISOTOPES

Strontium exists in the geologic formations in several isotopic species, with atomic numbers from 79 to 102, of which ⁸⁸Sr is the most abundant stable isotope. The ⁸⁷Sr to ⁸⁶Sr ratio is used in age determinations. The ⁸⁷Sr to ⁸⁶Sr ratio is typical for any geographical sites and therefore is proposed

as a tool to identify the geographic origin of ciders (Garcia-Ruiz et al., 2007). The ratio of these isotopes vary in principal contamination sources and can be used for tracing of industrial aerosol sources (Geagea et al., 2008).

Products of several nuclear processes are ^{89}Sr and ^{90}Sr the second radionuclide is considered to be one of the most biologically hazardous for the environment. Sources of ^{90}Sr are associated with nuclear reactions, and have been tracked since nuclear energy was used on the global and regional scales. During the period 1945–1980, radioactive Sr was released into the atmosphere mainly from above-ground detonations of nuclear weapons. Its continuous sources increased greatly after the Chernobyl accident in 1986, and its relatively long live ($t_{1/2}$ –29 years) may lead to steadily increasing concentrations in various environmental compartments.

Biogeochemical behavior of ^{90}Sr is similar to stable Sr. Its distribution has been recently monitored, particularly in the regions affected by the deposition of Chernobyl emissions. About a decade after that accident (1986–1995), mineral soils of Belarus, in the most affected area, contained ^{90}Sr at the range from 1.64 to 109 kBq/m². Alluvial and organic-rich soils accumulated higher amounts of ^{90}Sr , up to 340 Bq/kg, than light mineral soils. Soils of Tomsk (industrial region of Russia) contained this radionuclide, in the period of the 1990s, in the range of 111–121 Bq/kg (Rikhanov, 1997). Soils of Kazakhstan sampled in 1992 contained ^{90}Sr in the range of average values from 48 to 70 mCi/m² (Panin, 2004).

The speciation of this radionuclide in various soils of seminatural landscapes indicates that easily soluble fractions make up to 90% the total content, and are likely to occur as organic fractions in the soil solution (Agapkina et al., 1995; Korobova et al., 1998). The migration of this radionuclide in soil profiles is relatively extensive, but depends largely upon soil properties, and particularly on both kind and content of SOM. The migration velocity for ^{90}Sr has been calculated as 0.7–1.5 cm/year, but a great part of the residual ^{90}Sr still is located in the upper 10 cm soil layer (Arapis et al., 1997; Shagalova et al., 2000). Pavlotskaya et al.⁶⁰⁴ reported that easy coprecipitation of ^{90}Sr by hydrous Fe oxides leads to its accumulation in Fe-rich soil horizons. However, there also are information that this radionuclide is likely to occur in easily exchangeable forms and is characterized by relatively high migration (Kagan and Kadatsky,¹³⁶⁰ Kuzniecowa and Generalova¹³⁸⁴). The migration of this radionuclide in soil profiles is relatively high, especially in the floodplain where up to 30% of its content in the top soil layer is below 5 cm depth. In topsoil horizons along the Prypec River in Belarus, ^{90}Sr is concentrated up to 340 Bq/kg, and is reported to be also highly mobile.¹³⁸⁴

Plants easily absorb ^{90}Sr , similarly to the stable Sr, therefore this radionuclide is applied in studies of uptake and transport Sr in plants (Tsukada et al., 2005). Some plants are proposed for the use in phytoremediation; for example, alamo switchgrass (*Panicum virginatum* L.), can accumulate up to 44% of the total amount of this radionuclide from soils (Entry and Watrud¹²⁹²). Also *Amaranthus* species are reported to be effective in the phytoextraction of the radionuclide from soils, as has been investigated in the Chernobyl exclusion zone (Duschenkov and Sorochinsky¹²⁸³). The transfer factor (TF) for ^{90}Sr , expressed as its ratio in fresh weight plants to concentration in soils, varies highly, and has been calculated as follows: 0.4, for potato tubers; 0.8, for vegetable leaves; and 20, for vegetable roots (Kabata-Pendias and Pendias¹³⁵⁷).

The uptake of ^{90}Sr by plants depends upon the content of its easily mobile fractions in soils and on plant capability for uptake. Korobova et al. (1998) reported the following order of the radionuclide uptake by plants: legumes > herbs > grasses. Soils amendment with Ca, Mg, and K fertilizers inhibit its availability to plants.

III BARIUM

A INTRODUCTION

Barium is a common and quite ubiquitous element; its mean content in the Earth's crust amounts to 400 mg/kg, and ranges from 250 to 584 mg/kg in the upper continental crust (Tables 3.2 and 7.2).

Ba has a lithophilic affinity and is likely to concentrate in acid igneous and sedimentary rocks, ranging widely in various rocks from 50 to 1200 mg/kg. Its ionic radius is fairly similar to the ionic radius of K (Table 7.1), and thus usually follows the K fate in geochemical processes.

World mining of Ba, mainly from intrusions in granites and shale, was estimated as 2.9 Mt in 1995 (Reimann and de Caritat, 1998). Contents of Ba in coals range from 75 to 330 mg/kg, but in some lignite coal it can be concentrated up to 1420 mg/kg. Average Ba in coals in the United States is estimated as 170 mg/kg, but may reach the concentration up to 22,000 mg/kg (Finkelman, 1999). In crude oil, Ba ranges from 0.3 to 5 mg/kg.

The most common naturally occurring minerals are barite, BaSO_4 , and hollandite, $\text{Ba}_2\text{Mn}_8\text{O}_{16}$. Also the carbonate-Ba compound—whiterite, BaCO_3 , occurs relatively often. It may be present in some silicate minerals as impurities.

Industrial uses of Ba are quite variable. It is widely used in the production of brick, tile, glass, and ceramics. It is applied in the synthetic rubber industry. The use of Ba is broad in the chemical industry, especially for the paint production. The barite mineral, due to its relatively heavy weight, is used extensively (as a drilling mud) in oil- and gas-drilling fluids. Different Ba compounds also have several medical uses, including the x-ray examination.

B SOILS

During weathering, Ba is not very mobile because is easily precipitated as sulfates and carbonates, and also strongly adsorbed by clays. Its contents in surface soils are fairly similar to its distribution in parent rocks and vary from 10 to 1500 mg/kg, being the lowest in organic and the highest in loamy soils (Table 7.2). The reported Ba average range for soils on the world scale is from 362 to 580 mg/kg (Table 3.2).

Govindaraju¹³¹³ reported the Ba contents in reference soils from China to range within 180–1210 mg/kg, and in soils from the United States, to range within 290–2240 mg/kg. The high Ba content in Chinese soils is related to the Au ore field (Peters, 2002). Monitoring on 218 surface-soil samples from Poland gave the Ba range of 20–130 mg/kg and did not show any changes within the period 1995–2000 (Terelak et al., 2002). Swedish arable soils contain Ba in the range from 383 to 778 mg/kg, at an average value of 608 mg/kg (Eriksson, 2001). An interim soil quality criterion of 750 mg Ba/kg for agricultural soils has been established in Canada (Jaritz, 2004).

Although Ba is easily adsorbed, especially by oxides and hydroxides, it is relatively mobile in soils, particularly in acid ones. Its great affinity for the concentration in Mn soil nodules (up to 0.2%) and Mn soil minerals (up to over 5%) is an effect of easy displacement of other sorbed alkaline earth metals. Those metals, on the other hand, can also readily substitute for Ba in aluminosilicates.

Barium contents in soil solution show considerable variation, from 43 $\mu\text{g/L}$ in loamy soil to 307 $\mu\text{g/L}$ in sandy soil. Ba easily displaces other sorbed alkaline earth metals from some oxides (MnO_2 , TiO_2), but, on the contrary, is displaced from Al_2O_3 by alkaline earth metals (Be, Sr).⁹⁴⁸ Easily soluble mineral, hollandite, is often responsible for upwards migration of Ba in aridic soils, where it is known to concentrate at surface layer varnishes. However, in soils of temperate humid climate zones, Ba also can be fixed by Fe and Mn hydrous oxides and become immobile. Mica, especially coated with FA, reveals a great sorption capacity for Ba (Lee et al., 2007).

Barium from aerial sources and from P-fertilizers can influence a steady increase of this metal in soils of some regions. Thus, soils in surroundings of phosphate fertilizer plants have increased Ba levels in the surface layer (Turski et al.¹¹⁶⁹) In general, the input of Ba from aerial sources and P-fertilizers increases its output (leaching and plant uptake) and the Ba budget in rural soils shows a steady increase.

C PLANTS

Although Ba is reported to be commonly present in plants, it is apparently not an essential component of plant tissue. Ba mean contents in most plants range from 2 to 13 mg/kg, with an

TABLE 7.5
Barium in Food and Feed Plants^a (mg/kg)

Plant	Range	Mean
Wheat, grain ^b	—	3.2
Barley, grain ^b	—	5.1
Cereal, grains	4.2–6.6	5.5
Bean, seeds	1–15	8
Carrot, roots	2–50	13
Onion, bulbs	3–75	12
Potato	1.3–35	5
Lettuce, leaves	9–11	—
Cabbage, leaves	—	4.8
Tomato, fruits	2.3	2.1
Apple, fruits	1.5–2	1.5
Orange, fruits	—	3.1
Blueberries-R, fruits ^b	8–60	—
Blueberries-G, fruits ^b	132–181	160
Meadow clover ^c	—	12
White clover ^c	—	14

^a Data compiled by Kabata-Pendias, A. and Pendias, H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 400, 1999 (Po). Unless otherwise indicated.

^b Berries sampled in Russia—R, and in Germany—G, after Markert, B. and Vtorova, V. N., *Biol. Bull.*, 22, 453, 1995.

^c After Anke M., Jaritz M., Dorn W., et al. 2002. *Metal Elements in Environment, Medicine and Biology*, 5–28, Publ. House “Eurobit,” Timișara.

exception of blueberries in which highly elevated Ba levels are reported (Table 7.5). Much higher concentrations of Ba are also found in different trees and shrubs grown in area of arid climate. The highest contents of Ba are reported for Brazil nuts, depending on the location of growth, from about 3000 to 4000 mg/kg (Kabata-Pendias and Mukherjee, 2007).

Plants can take up Ba quite easily from acid soils, however, there are only a few reports on toxic Ba concentrations in plants, that is, the growth of barley and beans was inhibited in soil containing 2000 mg Ba/kg (Chaudry et al.¹³⁴). Possible toxicity of this element to plants may be reduced by the addition of Ca, Mg, and S salts to growth media, as effects of antagonistic interactions between these elements, but most probably due to the formation of slightly soluble BaCO₃ and BaSO₄.

Weinberg⁸⁵⁶ reported a high affinity of Ba²⁺ to be bound to the surface of yeast. There are not many reports on the Ba toxicity to plants. According to Suva et al. (2008) Ba at the concentration 5000 μM in the hydroponic culture inhibited photosynthesis and K transport in soybean plants. Ugany et al. (2000) proposed the LOEC value for Ba in bush beans as 700 and 460 mg/kg for primary and trifoliolate leaves, respectively.

IV RADIUM

A INTRODUCTION

Radium is a naturally occurring metal and is ubiquitous in all environmental compartments at very low concentrations. It exists mainly as divalent radioactive cation composed of several isotopes and

has chemical properties that are similar to Ba, Sr, and Ca (Table 7.1). It is a lithophilic element and occurs as impurities in several minerals of zeolite group, its typical mineral is radiobarite, (Ba, Ra) SO_4 . Ra may form several complex forms: RaOH^+ , RaCl^+ , RaCO_3° , and RaSO_4° .

Radium occurs in the environment as radioactive nuclides of which ^{223}Ra , ^{224}Ra , ^{226}Ra , and ^{228}Ra are the common products of the U and Th decay chains. Thus, the geochemistry of U and Th controls in what minerals Ra is likely to occur. ^{226}Ra is the most stable and relatively frequent radionuclide in the biosphere. Most data on the environmental distribution are for the ^{226}Ra , and its half-life time is estimated at 1599 or 1622 years.

The radionuclide ^{226}Ra is a natural component of the environment, and is also of the anthropogenic origin, mainly from phosphate and potassium fertilizer, radioactive wastes, luminizing wastes, coal combustion, and cement factories. Uranium mining and processing is also a significant source of Ra. The mean concentration of ^{226}Ra in coal is at the order of 1 pCi/g and soil surrounding coal-fired power plants contains elevated Ra levels up to 8 pCi/g (ATSDR, 2002).

Radium has been used as a radiation source for radiotherapy, for several nuclear facilities and in radiometric dating methods. Until the 1960s, Ra was a component of the luminous paints used for various instruments and painting (ATSDR, 2002).

B SOILS

Radium content in the continental crust is estimated as 0.9 ng/kg, its range in various rocks is between 0.1 and 1.1 ng/kg, and range in soils—between 0.03 and 1.6 ng/kg. Several data are presented on the ^{226}Ra activity levels in soils (range in Bq/kg): (1) 4.4–56.4 in soils of Canada (Zikovsky and Blagoeva, 1994), (2) 13.9–60.3 in soil of Japan (Uchida and Tagami, 2007), (3) 14.4–79.1 in farm soils of Sudan (Sam and Eriksson, 1995), and (4) mean 150 in soils of Turkey (Akyil et al., 2002). Increased levels of ^{226}Ra is also reported for soils of forest land in New England (Langley-Turnlaugh and Evans, 2000). Ra contamination of soils in large flooding zones in Belgium is due to discharged waste water from a phosphate plant (Paridaens, 2008).

There are observations that soils formed on some limestones, argillaceous limestones in particular, have accumulated significant amounts of Ra. Behavior of ^{226}Ra is associated with Ca, Mg, and Al in soils (Vandenhove et al., 2005). Also SO_4^{2-} has a significant impact on this radionuclide leachability (Pulhani et al., 2007). Megumi and Mamuro⁵²⁹ studied the concentrations of U-series nuclides in soils derived from granites and found that they increase with decreases in particle size (Figure 7.2).

SOM and Fe/Mn-hydroxides, as well as clay minerals, have a strong affinity for Ra and significantly decreases its exchangeable fraction, especially near neutral and alkaline pH conditions (Greeman et al., 1999). Zhang et al. (2002) suggest that Ra can form complexes on the clay surface and also within inner space.

The Ra sorption highly vary; the K_d (ml/g) values for various soils is given within the range 57–530,000, with the lowest values for sandy soils (Smith and Amonette, 2006). These authors emphasized that the influence of bacteria, plants, and animals have a serious impact on the Ra mobility. Especially sulfate-reducing bacteria can produce rapid dissolution of RaSO_4 in sludge under reducing conditions. Thus, Ra mobility is enhanced under anaerobic conditions (Landa, 1996; Pardue and Guo, 1998) and in very acidic soils, ranging from about 1% to 10% of its content in surface soils (Taskayev et al.⁷⁷³). In moist soils, the mobility and bioavailability of Ra highly increases (Matthews et al., 2006).

C PLANTS

The content of Ra in plants is roughly estimated as 0.03–1.6 ng/kg (Bowen⁹⁴). Plants grown on soil with ^{226}Ra at 8.48 Bq/kg, and exchangeable fraction at 0.62 Bq/kg, contained this isotope in the range from about 30 to above 1000 mBq/kg (Kabata-Pendias and Pendias¹³⁵⁷).

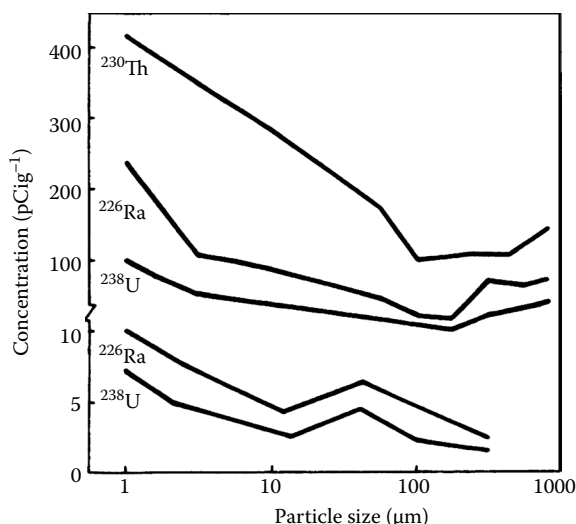


FIGURE 7.2 Concentration of some radionuclides in soil particle size from the B horizon of soils derived from two different granites in Japan. (Modified from Megumi, K. and Mamuro, T., *J. Geophys. Res.*, 82, 353, 1977.)

Radium is relatively easily taken up by plants, mainly through the root system, and also easily pass through the shoots (Gunn and Mistry, 2005). However, its phytoavailability is highly dependent on the specific plant species and soil conditions. Especially soil properties, CEC and SOM, affect soil–plant TF (Vandenhove and van Hees, 2007). Soil–plant TF may range from 0.001 to 6.5, being lower for fruits than for grain (Rayno *vide* ATSDR, 2002). The order of the TF from soil to plants is, as follows: leaf-vegetables > root-vegetables > grasses > corn stems > grains (Rosiak and Pietrzak-Flis, 1998). Uchida and Tagami (2007) studied the uptake of this radionuclide by vegetable crops and calculated the TF values from $<1.1 \times 10^{-3}$ to 5.8×10^{-2} with the geometric mean of 6.4×10^{-3} , the lowest value is for potato and the highest for leek (green). Also low TF values were found for barley and wheat. According to data reported by these authors, ^{226}Ra concentrations highly vary in crop plants, from <0.015 Bq/kg in barley to 1.431 Bq/kg in carrot.

Plants growing on soils with ^{226}Ra activities from 0.7 to 23 Bq/kg reveal the activity from 0.1 to 7.6 Bq/kg, in vegetative and edible crop parts, respectively (Sam and Eriksson, 1995). The concentration of ^{226}Ra in vegetables collected in Poland during the period 1995–1996 varied from 0.087 (cucumber) to 0.594 (carrot) Bq/kg. (Rosiak and Pietrzak-Flis, 1998). The uptake and distribution of Ra in plants is influenced by some chelators, for example, EDTA and citrate (Smith and Amonette, 2006).

8 Elements of Group 3 (Previously Group IIb)

Geochemical and biochemical properties of the elements of Group 3, as well as their abundance in the biosphere are highly divergent. Two elements, scandium (Sc) and yttrium (Y) are rather rare in the environment, and usually exhibit the affinity for oxygen and their oxidation state is mainly +3 (Table 8.1). Two other elements, lanthanum (La) and actinium (Ac) are associated with two subgroups of elements: lanthanides and actinides, of which many elements are either natural or artificial radionuclides.

I SCANDIUM

A INTRODUCTION

Crustal average content of Sc is estimated at 11 mg/kg (Table 3.2), while other sources yielded values from 16 to 30 mg/kg (Table 8.2). Sc is also likely to occur in higher amounts in mafic igneous rocks and in argillaceous sediments (Table 8.2). In nature, it occurs mainly as Sc^{3+} which can substitute for Al^{3+} , Fe^{3+} , and also Ti^{3+} . It is mainly associated with ferromagnesian minerals and biotite, and is also reported to be enriched, up to 36 mg/kg, in some phosphorites. Its mineral, rarely occurring thorveitite, $\text{Sc}_2(\text{Si}_2\text{O}_7)$, is the primary source of Sc.

Some organic raw materials as peat, coal, and crude oil can accumulate increased levels of Sc (5–100 mg/kg AW), and thus their combustion can be a source of environmental enrichment of this metal⁸⁵⁵. In the United States, the mean concentration of Sc in coal is 4.2 mg/kg, but may reach up to 100 mg/kg (Finkelman, 1999).

Scandium is obtained as by-product at uranium explorations and used mainly for lasers, lightening, and fluorescent materials (high intensity lights, color television). It is dumped mainly by petrol-producing industries. Reimann and de Caritat (1998) estimated its annual production at 537 kt.

B SOILS

The average contents of Sc in soils worldwide are estimated at 11.7 mg/kg (Table 3.2) and the range between 0.8 and 28 mg/kg. The soil Sc is governed mainly by the parent material, being the lowest in light sandy soils. Higher amounts are in heavy loamy soils, especially those that are derived from granitic and volcanic rocks (Table 8.2).

Govindaraju¹³¹³ reported Sc to range from 5 to 28 mg/kg in the reference soils of China, and from 5 to 18 mg/kg in soils of the United States. Soils of San Joaquin Valley of central California contain Sc within the range 9.2–12 mg/kg and its distribution did not show any relation to contamination of soils (Wilson et al., 1994). Erdman et al.²¹⁸ calculated the mean Sc content of uncultivated soils in the United States to be 7.1 mg/kg and in cultivated soils to be 5.1 mg/kg. Laul et al.⁴⁶² estimated the range of Sc concentration in soils as 2.9–17 mg/kg. In agricultural soils of Japan, its median concentrations vary from 13 to 28 mg/kg in Acrisols and Andosols, respectively (Takeda et al., 2004). Swedish arable soils contain Sc in the range from 3.5 to 16 mg/kg, at an average value of 10 mg/kg (Eriksson, 2001). The content of Sc in soils of industrial region of Poland range from 0.53 to 7.78 mg/kg and is higher than in the rural region (Połedniok, 2008). Waganov and

TABLE 8.1
Selected Properties of Scandium and Yttrium

Element	Atomic Number	Atomic Mass	Atomic Radius (pm)	Density (20°C) (g/cm ³)	Valence
Sc, scandium	21	44.96	88.5–102	2.9	+3
Y, yttrium	39	88.91	104–121.5	4.4	+3

Nizharadze¹¹⁸⁴ estimated 5 mg/kg for the mean Sc concentration in deep loess deposits of the European part of Russia.

Scandium is likely to form complexes such as $\text{Sc}(\text{H}_2\text{O})_6^{3+}$ and $\text{Sc}(\text{H}_2\text{O})_5\text{OH}^{2+}$ in aqueous phases, and also shows an affinity for complexing with PO_4 , SO_4 , CO_3 , as well as with some organic compounds. Phosphate fertilizers contain relatively high amounts of Sc, in the range of 7–36 mg/kg, and may elevate its concentration in surface agricultural soils.

C PLANTS

There is a paucity of data on the Sc distribution in plants. Connor and Shacklette¹⁴⁵ estimated the mean content of Sc in some shrubs and trees as <5 mg/kg AW and reported that in about 3% of the analyzed samples Sc was at detectable concentrations. Duke¹⁹⁷ estimated Sc to range from 0.002 to 0.1 mg/kg in several food plants of the tropical forest region. Laul et al.⁴⁶² found 0.005 mg/kg Sc in vegetables and 0.07 mg/kg in grass. Sc content of mosses from Scandinavia varies from 0.16 to 0.25 mg/kg, with the lowest value from Sweden and the highest from Denmark.¹¹³⁵ Bowen⁹⁴ reported the range of Sc in lichens and bryophytes to be from 0.3 to 0.7 mg/kg, whereas in fungi the amounts of Sc were lower, from <0.002 to 0.3 mg/kg.

Yoshino and Goto¹¹⁹² found 0.174 mg/kg Sc in rice straw and 0.998 mg/kg Sc in manure produced from that straw. Ozoliniya and Kiunke⁵⁸⁸ reported high concentrations of Sc in barley roots (up to 0.63 mg/kg) and observed that the greatest amounts of Sc were taken up by plants from sandy

TABLE 8.2
Abundance of Scandium and Yttrium in Rocks and Soils (mg/kg)

Environmental Compartment	Sc	Y
Earth's crust	16–30	20–33
Igneous rocks	—	—
Mafic	5–35	0.5–20
Acid	3–15	20–33
Sedimentary rocks	—	—
Argillaceous	10–15	25–40
Sandstones	1–3	15–250
Calcareous	0.5–5	4–30
Soils ^a	9.5	12
Arenosols (sandy)	0.8–14	3–28
Podzols (medium loamy)	3–8	7–30
Cambisols (heavy loamy)	2.5–28	7–60
Calcisols (calcareous)	6–11	—
Histosols (organic)	5–20 ^b	—

^a Soil groups are given according to the WBR (Table 3.1).

^b Data for forest soils.

soils. The Sc contents seemed to be higher in old leaves than in young leaves, and its highest concentrations (0.014–0.026 mg/kg) were reported for flax plants, while in lettuce leaves Sc ranged from 0.007 to 0.012 mg/kg. Shtangeeva et al. (2004) studied the uptake of Sc by wheat seedlings and observed increased Sc contents during germination of seeds and in roots. Some interactions between Sc and Na, K, Ca, and Zn were noticed in different parts of the seedlings.

Relatively high levels of Sc were found by Inarida et al.¹⁰³² in tea leaves from different countries within the range 0.013–0.14 mg/kg, and average 0.037 mg/kg.

II YTTRIUM

A INTRODUCTION

The occurrence of Y in the Earth's crust is estimated within the range of 20–33 mg/kg (Table 8.2) and fairly uniform in different rocks (being somewhat smaller in mafic rocks (0.5–20 mg/kg) than in acid rocks (20–33 mg/kg) and sandstones (15–250 mg/kg). Geochemical behavior of Y is very similar to the alkaline earths and other rare earth elements (REEs) and, particularly to lanthanides. Thus, its higher contents are associated with minerals that concentrate REEs. Yttrium exhibits lithophilic affinity, has the oxidation state +3 (Table 8.1) and is incorporated, together with REEs, in several minerals, such as: oxides, carbonates, silicates, and phosphates (e.g., xenotime, YPO_4 ; fergusonite, YNbO_4). Minerals of Y are associated mainly with monazite veins and pegmatites.

Contents of Y in coal range from 7 to 12 mg/kg and does not indicate its sorption by organic substances, although in some coal samples it may reach up to 170 mg/kg (Finkelman, 1999). In fly and bottom ashes it is concentrated to about 44 mg/kg (Llorens et al., 2000). The Y content of nitrogen fertilizers is given in a range of 2–4 mg/kg.¹³⁶²

Global production of Y (as Y_2O_3) is calculated at 8.9 kt for 2008 (USDI, 2009). It has a relatively broad industrial application in ceramic and glass industries, high-temperature bricks, laser, color monitors, and various catalysts (e.g., in the production of plastics). Some Y compounds have luminescence properties and are used for various lasers.

B SOILS

Average contents of Y in worldwide soils is estimated at 12 mg/kg and range between 7 and 60 mg/kg, being the highest heavy loamy soils (Table 8.2). The most comprehensive data are reported for Y in soils of the United States and give the range of average contents from 16 to 33 mg/kg. The highest contents (up to 150 mg/kg) have also been cited for various soil groups (Shacklette and Boerngen⁷⁰⁶). Data of other authors, however, yielded smaller amounts of Y in soils of various countries, within the general range of <2–70 mg/kg. The average contents of Y in reference soils range from 22 to 24 mg/kg, for China and the United States, respectively (Govindaraju¹³¹³). In Japanese agricultural soils median contents of Y varied from 8.8 to 24 mg/kg, in Acrisols and Andosols, respectively (Takeda et al., 2004). Soils of San Joaquin Valley of central California contain Y in the range between 17 and 27 mg/kg, being the highest in contaminated sites (Wilson et al., 1994). Gough et al.¹⁰¹² found Y in various soils of Alaska to range from <4 to 100 mg/kg, with a mean of 14 mg/kg. Similar values for Y in soils are given by Ure and Bacon⁸¹⁸ for Great Britain (22 mg/kg), by Duddy¹⁹⁶ for Australia (17 mg/kg), and by Dobrowolski¹⁸¹ for Poland (10 mg/kg in sandy soil). Swedish arable soils contain Y in the range of 9–41 mg/kg, at an average value of 27 mg/kg (Eriksson, 2001). Sandy soils of Poland contain Y in the range from <2 to 17 mg/kg (mean 4.8) and loamy soils from 7 to 19 mg/kg (mean 12.4) (Dudka, 1992). Yoshino and Goto¹¹⁹² found Y within a range of 5.3–17.1 mg/kg in Japanese soils. Govindaraju¹³¹³ has reported results for Y in reference soils of China that range from 11 to 39 mg/kg (mean 22 mg/kg), and of the United States, from 16 to 40 mg/kg (mean 24 mg/kg).

C PLANTS

The reference content of Y in plants is calculated at 0.02 mg/kg (Markert^{1399a}). However, results of various analysis showed quite variable amounts for Y in plants, in the range from 0.01 to 3.5 mg/kg, depending on soil and climatic factors (Kabata-Pendias and Mukhejee, 2007).

Yoshino and Goto¹⁹² found Y in rice straw at the level of 0.061 mg/kg, while in manure produced from that straw, Y content increased up to 0.73 mg/kg. Mean Y contents of Swedish wheat and barley grains are 0.79 and 1.3 µg/kg, respectively (Eriksson, 2001).

Relatively high contents of Y are reported for mosses and lichens. The data for Y in these plants, collected in 1970 in Scandinavia, range from 0.2 to 2.0 mg/kg, whereas in bryophytes its concentrations range from 1.3 to 7.5 mg/kg.²¹⁷ Mosses collected during the period 1990–1995 contained fairly similar amounts of this element, within the range 0.04–2.3 mg/kg (Berg and Steinnes¹²²³). Increased levels of Y in mosses and lichens, as compared with higher plants, clearly indicate that main source of this metal is atmospheric deposition.

III LANTHANIDES

A INTRODUCTION

The terms Rare Earth Elements (REE) or Rare Elements (RE) commonly used in the literature are confusing since they refer to different elements, depending on the author. Usually, REEs are related to the Lanthanide Series distinguished in the Periodic Table of Elements. However, the IUPAC proposed to add to the REEs also other elements, yttrium and scandium. To avoid any confusion, the term Lanthanides (LA) will be used for the elements from La through Lu (the IUPAC proposed the term Lanthanoids, Ln).

Lanthanides (LAs) comprise the group of 15 elements (Table 8.3), of which only one, promethium (Pm) does not occur naturally in the Earth's crust (with an exception of very small amounts in U ores), while the other 14 are relatively abundant in rocks and soils (Table 8.4). The terrestrial distribution of the LAs shows a general peculiarity; their contents decrease with an increase in atomic weights, and, according to the Oddo–Harkins rule, the element with the even atomic

TABLE 8.3
Selected Properties of Lanthanide Elements (Natural)

Element	Atomic Number	Atomic Mass	Ionic Radius (pm)	Oxidation State ^a	Density (g/cm ³)
La, lanthanum	57	138.9	117	+3	6.15
Ce, cerium	58	140.2	115	+3 , +4	6.77
Pr, praseodymium	59	140.9	113	+3 , +4	6.77
Nd, neodymium	60	144.2	143	+2, +3, +5	7.00
Sm, samarium	62	150.4	135	+3 , +2	7.52
Eu, europium	63	151.9	131	+3 , +2	5.24
Gd, gadolinium	64	157.3	108	+3 , +2, +1	5.90
Tb, terbium	65	158.9	106	+3 , +4	8.23
Dy, dysprosium	66	162.5	121	+2, +3, +4	8.55
Ho, holmium	67	164.9	104	+3	8.79
Er, erbium	68	167.3	103	+3	9.06
Tm, thulium	69	168.9	117	+3 , +2	9.32
Yb, ytterbium	70	173.0	116	+3 , +2	6.97
Lu, lutetium	71	174.9	100	+3	9.84

^a Valence values in bold are for the main oxidation states.

TABLE 8.4
Abundance of Lanthanides in Environment (mg/kg)

Environmental Compartment	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Earth's crust	30	60	8.2	28	4.7	1.2	5.4	0.6	3.7	0.8	2.8	0.5	2.2	0.3
Igneous rocks														
Mafic	2–70	4–60	1–15	2–30	0.1–1.7	0.01–4	0.1–8	0.1–1.2	0.05–7	0.1–1.5	0.1–1	0.1–0.6	0.1–3.5	0.1–0.6
Acid	30–150	20–250	6–30	18–80	6–11	1–2	4–10	1–2.5	5–8	1.3–2	3.4–4.7	0.3–0.7	3–4.5	0.5–1.2
Sedimentary rocks														
Argillaceous	30–90	3–90	6–10	18–35	5–7	1–2	5–7.5	0.9–1.1	4–6	1–1.8	2.5–4	0.2–0.6	2.2–4	0.2–0.7
Sandstones	17–40	25–80	4–9	16–48	4–10	0.7–2	3–10	1.6–2	2.6–7.2	0.05–2	1.5–6	0.3–0.7	1.2–4.4	0.8–1.2
Calcareous	4–10	7–20	1–2.5	5–9	1–2	0.2–0.4	1.3–2.7	0.2–0.4	0.8–2	0.2–0.3	0.4–0.7	0.03–0.2	0.3–1.6	0.003–0.2
Soils^a														
Arenosols (sandy)	0.9–3.5	8.4–21	1.4	3.6–7	0.7–3.5	0.2–0.6	0.7–5	0.2–0.5	0.8–5	0.2–1.1	0.3–1.7	0.4–0.5	0.4–1.5	0.05–0.3
Podzols (medium loamy)	5–21	44–56	5.5–6.2	18.7–26	3.5–6.3	1.3–1.5	4–5.9	1.0–1.2	3.6–5	1.1–2	2.1–2.3	0.4–0.6	2.3–2.8	0.4–0.5
Cambisols (heavy loamy)	20–36	32–64	13–15	18.2–31	3.4–5.9	0.6–1.7	6–15	0.7–1.4	7–11	1–2	1.7–4.8	0.5–0.8	1.3–3.3	0.2–0.5
Calcisols (calcareous)	—	—	—	—	—	—	—	—	—	—	0.5–0.8	—	—	—
Histosols (organic)	1.4–9.2	2–42	7.7	1–1.2	0.3–5.7	0.03–1.9	3.6–4.7	0.04–0.9	4.7	0.8	2.05	—	0.1–2.0	0.01–0.29

^a Soil groups are given according to the WBR (Table 3.1).

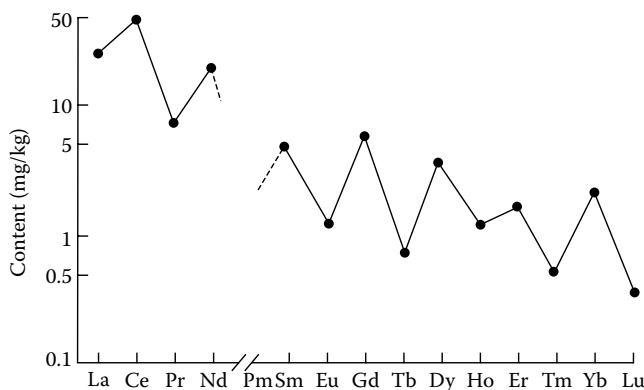


FIGURE 8.1 Average contents of LAs in surface soils. [Prometium (Pm) does not occur in the natural environment]. (From Kabata-Pendias A., Mukherjee A. B. 2007. *Trace Elements from Soil to Human*. Springer, Berlin (Figure II.3.1). With permission.)

number is more frequent than the next element with an odd atomic number. This rule governs also the distribution of all elements in the universe, but is much less pronounced than in the case of LAs. Although several factors influence the abundance of lanthanides in soils, this rule can also be observed in average contents of LAs (Figure 8.1).

Two subgroups of LAs are distinguished: the first composed of the more basic and more soluble, light rare elements (LREs), from La to Gd, more basic and more mobile than metals of the second group, heavy rare elements (HREs), from Tb to Lu. Some authors have distinguished also a medium weight group: MHs obtaining elements from Sm to Ho (Xu et al., 2002). During weathering processes, the LAs are fractionated. Their enrichment in weathered material is relatively high, especially for the light elements' subgroup.¹⁹⁶

LAs are constituents of several different minerals and also are likely to be concentrated in phosphorites being incorporated in relatively common minerals such as: monazite (monacite), $(La, Ce, Th)PO_4$; bastnasite, $(CeF)CO_3$; cheralite, $(Ce, La, Y, Th) PO_4$; and xenotime, YPO_4 .

Common mineral, monazite, is often associated with phosphatic rocks what resulted in elevated amounts of some LAs in phosphorus fertilizers (Table 2.7). Christensen et al. (2004) studied the LAs in 70 natural calcite samples and found the variation in the distribution of light and heavy Als depending upon the origin of calcite. Most often, their lowest concentrations are reported for ultramafic and calcareous rocks. Organic compounds play a significant role in the distribution of LAs and affect their increased levels in humus horizons of soils and in forest-soil litter.

Global production of REE (LAs) is given as 124 kt in 2008 (USDI, 2009). Two major sources of LAs, and in particular of Ce, for the commercial production, are monazite, and bastnasite. Monazite, associated with granites and gneisses, is especially resistant to weathering and is concentrated, by sedimentary processes, often in beach sands.

The use of LAs is relatively broad in various industries from glass production (mainly as colorants) to sophisticated electronic devices, as well as to catalytic converters, metallic alloys, rechargeable batteries, radars, etc. Cerium is added to diesel fuel for lowering the soot ignition temperature and is relatively slightly trapped by filter (Ulrich and Wichser, 2003).

B SOILS

The distribution of LAs in different soils is quite similar when compared mean values after various authors and shows the relation to the geological origin of parent rocks and their mineral composition. In most cases their lowest values are for sandy soils, and the highest for loamy soils (Tables 8.4 and 8.5). Sonke and Salters (2006) described the important role of HS (humic substances)

in the LAs fractionation during weathering and transport at the Earth's surface. Binding activity of HS and especially of DOM toward the LAs is affected by pH values.

Acid soils contain usually less the LAs than alkaline soils, most probably due to easy removal of soluble hydroxide complexes. However, the LAs contents of different soils are fairly similar and indicate a strong positive relation between several LAs (mainly La, Ce, Pr, Nd, Sm) and fine soil granulometric fractions (Chojnicki¹²⁵⁶). Usually light LAs (LREs) are more abundant in soils than heavy LAs (HREs). For example, Zhu et al. (1997) reported that LREs range in soils of China range from 76.2 to 447.7 mg/kg, whereas HREs range from 9.2 to 55.2 mg/kg.

Heavy LAs are likely to concentrated in clay fraction (<0.002 mm) more than light LAs. In general, LAs due to the affinity to SOM, are about ten times more abundant in peat than in surrounding mineral soils. Various humic substances reveal the affinity to complex LAs and have impact on their behavior in soils and sediments (Stern et al., 2007). Lieth and Markert¹⁰⁶³ compared the chemical composition of peats and nearby mineral soils and estimated the range for LAs from 0.X to X0 mg/kg in both kinds of soils. Most of these elements are about 10 times more abundant in peat than in mineral soils. Stern et al. (2007) confirmed the affinity of humic substances for LAs in laboratory experiment. Markert¹⁰⁸⁵ found that the distribution pattern of the LAs in both soils follows that in geological samples and concluded that the Earth's crust is the original source of these elements in soils. In most soils, the LAs are likely to be concentrated in the amorphous Fe-oxide-bound fraction (Hu et al., 2006). In some soils, for example, Andosols, Ferrasols, Leptosols, the LAs might be accumulated in the residual fraction, associated with oxides, phosphates, carbonates, and silicates. Hu et al. (2006) reported that LAs with an odd atomic number are likely to predominate in water soluble and exchangeable fraction.

TABLE 8.5
Average and Range Contents of Lanthanides in Soils (mg/kg) and in Soil Leachates (ng/L)

Element	A	B	C	D	E	F
La	8.4–31.4	24.6–46.9	15.38	35.2	33	5.5–33.2
Ce	15.8–64.4	42.7–81.7	60.49	97.4	60	11–68
Pr	1.5–5.0	<9–11.5	4.13	8.4	7.7	1.3–7.5
Nd	7.6–28.6	16.9–29.1	14.63	29.3	29	0.3–53
Sm	1.8–4.0	4.5–8.6	2.76	5.5	4.5	0.9–4.6
Eu	0.44–1.43	0.89–1.20	0.64	0.8	0.8	0.22–0.83
Gd	1.77–4.54	<25	2.58	4.8	3.4	1.0–4.8
Tb	0.27–0.83	0.49–0.92	0.43	0.6	0.5	0.15–0.65
Dy	1.68–4.68	—	2.06	2.9	4.1	0.9–3.74
Ho	0.36–0.95	0.71–1.59	0.21	0.5	0.9	0.20–0.74
Er	1.1–2.72	—	0.79	1.4	2.2	0.63–2.2
Tm	0.16–0.40	0.37–0.66	0.08	0.2	0.3	0.09–0.33
Yb	1.11–2.64	1.92–3.88	0.57	1.1	2.9	0.60–2.3
Lu	0.16–0.40	0.29–0.55	0.08	0.2	0.4	0.09–0.34

Note: A—Range of means for 77 soils of Japan. (After Yoshida, S., et al., *Environ. Intern.*, 24, 275, 1998)¹⁵⁶⁶; B—Range for five soil samples of Czech Republic (Kučera J., Mizera J., Randa Z., Vávrová M. 2007. *J. Radioanal. Nucl. Chem.* 271:581–587); C—Mean values for nine topsoil samples of Australia (Diatloff E., Asher C.J., Smith F.W. 1996. *Austr. J. Soil Res.* 34:735–747); D—Data for 27 soils of China. (After Zhu J., et al., *Proc. 4th Int. Conf. Biogeochem. Trace Elements*, Berkeley, CA, June 23–26, 1997, 301)¹⁵⁷⁷; E—Mean value for topsoil samples of Sweden (Eriksson J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm); F—Range for 30 forest topsoil samples of Sweden (Tyler G. 2004. *Plant Soil* 267:191–206).

^a bdl = below detection limit.

Microorganisms reveal an impact on the behavior of LAs in soils, especially on their interaction with organic ligands (Ozaki et al., 2006). Perelomov and Yoshida (2008) studied the effect of bacteria (*Rhodopseudomonas pallustris*) on the LAs sorption, and noticed an increased sorption by quartz from about below 0.5% to about 1.5% of added elements, and by goethite, from below 0.5% to 3.5–4% of added elements (Figure 8.2). The authors concluded that the increased concentration of LAs in nonexchangeable states on mineral surface is due to the formation of low-soluble complexes with organic substances produced by bacterium.

All LAs are slightly mobile in soils. Their extractability with chelating agents (e.g., EDTA) is low and does not exceed 10% of the total contents (Zhu et al.,¹⁵⁷⁷ Wytenbach et al.¹⁵⁵⁶). The global mobility of LAs, calculated as the ratio of water-dissolved concentrations to those of the upper continental crust is relatively low; at about 0.01 ratio value (Gaillardet et al., 2003). The relative highest extraction was observed for Sm, Eu, Tb, and Nd. However, during a longer period of time, the mobility of LAs can affect their distribution. Öhlander et al.¹⁴⁴⁶ reported that since the last glaciation period (about 8700 years ago), up to 84% of LREs and 79% of HREs were leached down from soil derived from glacial till. The mobility of LAs in soils is variable, however, in humid climate conditions their losses from surface layer, due to both weathering and leaching processes, are observed (Tyler, 2004). Variable patterns of LAs mobility under the impact of soil pH are observed (Tyler and Olsson, 2001). According to these authors, the proportion of the LAs and Y concentrations in soil solution to their total amounts in soils corresponds to about $1:5 \times 10^4$. Mourier et al. (2008) observed that LREs distribution in soil profiles is affected by both weathering and leaching processes.

Agricultural use of LAs amendments is relatively common in China and some compounds have been widely applied to agricultural crops (Ding et al., 2006). Xu and Wang (2001) concluded that currently applied doses of LAs, at <230 g/ha/year do not affect the N oxidation and mineralization processes in soil. Results presented by Chu et al. (2007) indicate that La added to soil decreases the amount of microbial biomass and change the pattern of microbial utilization of glucose C. The LAs applied to soils are likely to be bound, preferable to SOM, oxides, and clay minerals. Hu et al. (2006) reported that less than 95% of the added LAs were adsorbed and not easily soluble. The LAs are commonly found in sewage sludge and manure at quite high amounts, fairly similar to their abundance in soils (Table 8.6). Thus, these amendment materials as well as phosphate fertilizers might be concerned as their source in cultivated soils. The application of LAs to agricultural soils

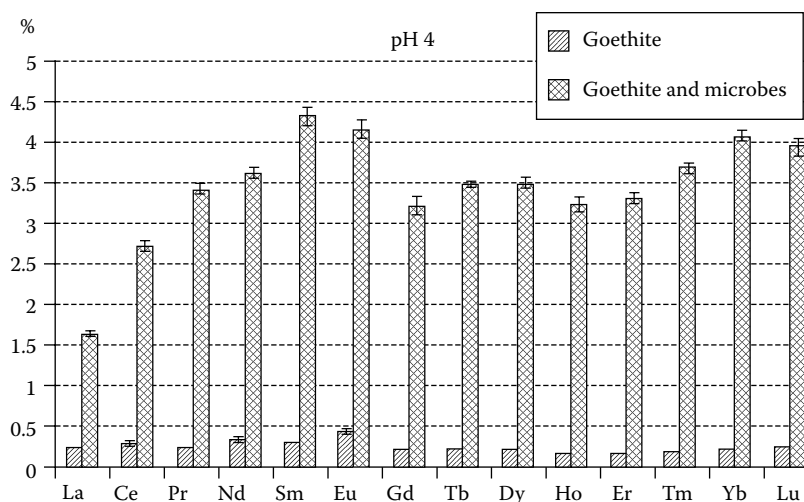


FIGURE 8.2 Sorption of LAs by goethite without and with microorganisms, at pH 4, in percents of added elements. (From Perelomov L.V., Yoshida S. 2008. *Water Air Soil Pollut.* 194:217–225 (Figure 2B). With permission.)

TABLE 8.6
Average Contents of Lanthanides in Sewage Sludges and Farmyard Manure (mg/kg)

Element	Sewage Sludges		Stable Manure		Cow Manure ^a
	United States ^a	Sweden ^b	United States ^a	Sweden ^c	
La	2.7	16	24	110	24
Ce	41.9	24	55	180	55
Pr	4.3	2.8	11	22	11
Nd	2.5	11.3	2.5	78	2.5
Sm	3.5	1.8	5.2	14	5.2
Eu	3.7	0.3	0.7	2.9	0.7
Gd	6.8	2	1.5	13	1.5
Tb	1.4	0.3	0.3	2	0.3
Dy	0.7	1.7	1	10	1
Ho	0.32	0.4	0.4	2.1	0.4
Er	1.16	1	0.7	5.9	0.7
Tm	0.39	0.2	0.1	0.8	0.1
Yb	0.6	1.1	1.8	5.4	1.8
Lu	0.12	0.2	0.6	0.8	0.6

^a After Furr, A. K., et al., *Environ. Sci. Technol.*, 10, 683, 1976.

^b Unweighted mean value. (After Eriksson, J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm.)

^c Element's contents given in mg/(kg P). (After Eriksson J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm.)

should be carefully investigated and discussed from both side of view: effects on soil fertility and the transfer to food plants. Elevated content of radiocesium (^{137}Cs), ranging from 33,000 to 68,500 Bq/m², is in soils contaminated by weapon plant in the vicinity of Tomsk-Seversk, Siberia (Gauthier-Lafaye et al., 2008).

Elevated concentrations of some lanthanides (La, Ce, Sm, Eu, and Tb) found in the air of industrial and urban areas (Table 2.2) indicate that these elements are likely to be released into the environment mainly from coal burning and nuclear energy materials processing. Also refining and petrochemical industries are known to be a source of LAs enrichment in ambient fine particles (Kulkarni et al., 2006). Urban pollution is a serious source of the LAs, and several times an increase in their concentrations in soils of downtown of Warsaw as compared with suburb areas (Zimny and Korzeniewska, 1996) is observed.

C PLANTS

Neither the LAs contents of plant tissue nor their physiological functions have received much attention until the last decade. Recently, more environmental studies on LAs have been performed.^{1446,1554–1556,1576} Robinson et al.¹¹²⁹ reported, as one of the first, high concentrations (up to 2300 mg/kg) of the total LAs in hickory trees and pointed out the similarity between their contents in tree leaves and in their exchangeable species in soil. Laul et al.⁴⁶² calculated the relative abundance of LAs in both soil and plants and showed that concentrations of these elements in plants followed their occurrence in soil. Orders of the LAs content in plants decrease with increase in the atomic number (Table 8.7). Woody plants seem to have the highest ability to absorb lanthanides, and hickory trees are most often reported as LAs-accumulating plants.

Concentrations of the LAs in plants vary within a broad range, from below 1 ppb to above 15,000 µg/kg. The distribution pattern somehow follows the Oddon–Harkins rule, and therefore

TABLE 8.7
Lanthanides in Terrestrial Plant Species (mg/kg AW)

Element	Woody Plants, United States ⁷¹⁰	Lichens and Mosses, Finland ²¹⁷	Horsetail, Finland ²¹⁵	<i>Acer pseudoplanatus</i> , Leaves (µg/kg DW) ¹⁵⁵⁶
La	30–300	13–150	1–30	1878
Ce	—	9–280	1–90	3426
Pr	700	1.2–31	0.5–6	—
Nd	—	8–150	3–50	1797
Sm	200–700	2–40	2–4	459
Eu	—	1–8.7	1–2	92.5
Gd	<100–300	2–28	3–8	—
Tb	—	0.3–3.3	1–2	70.3
Dy	50–300	1.3–26	2–9	—
Ho	150	0.2–4.5	1–2	—
Er	<100–300	0.6–13	2–7	—
Tm	—	0.07–2.2	1	—
Yb	300	0.5–26	1–2	152
Lu	—	0.05–2.2	—	15.8

Markert¹⁰⁸⁵ concluded that it might be possible to calculate the concentration of an unknown LA element once the relationships of elements to each other are known. Mosses, lichens, and bryophytes are known to accumulate higher amount of LAs than other plants. Rühling et al.¹¹³⁵ reported in mosses of Scandinavian countries the range for La (in mg/kg AW) from 0.35 to 1.84, and for Sm from 0.05 to 0.22. Plant sampled in 1999 along highways in Germany contained (in µg/kg): La, 53–380; Ce, 110–820; and Nd, 48–330. Always the highest concentrations were in dandelion (Djingova et al., 2003).

Li et al. (2001) reported that the availability of LAs to crop plants correlates well with their 0.1 M HCl soluble pool. According to Fang et al. (2007) soil pH and amorphous Fe oxides increased the LAs content of wheat roots, whereas LAs content of wheat shoots was independent of any soil properties. These authors concluded that the DTPA extraction method is the best for estimating bioavailability of LAs to wheat.

Although there are some other reports on stimulating impact of LAs on several processes in plants such as, seed germination, root growth, nodulation, chlorophyll production, these elements have not been proved yet to be essential to plants. According to Wang et al. (2006) the LAs should be studied as factors in antagonizing some trace metals and degradation of organophosphorus pesticide for guaranteeing food security in the future.

Shtangeeva and Ayrault (2007) reported that Eu added to a nutrient solution at the concentration of 0.01 mg/L disturbed the mineral balance in the plant tissues. The synergic effect of Eu + Ca on the yield and increased Eu level in wheat seedlings needs to be understood. Zhu et al.¹⁵⁷⁵ investigated the impact of La on physiological activities in the seedling stage of wheat. The inhibition of seed germination was observed at the La concentration higher than 200 mg/L in Hoagland solution. Some authors (Liu¹⁰⁶⁷, Xijie et al.¹¹⁸⁸) reported good effects of the addition of LAs on plant growth and yield. These authors, however, have not specified compounds of LAs used for the experiments, and have not discussed a possible function of these elements in plant metabolism. Dai et al. (2008) observed an impact of Ce on increased metabolic activity of mitochondria isolated from rice, and thus increased rice growth. Elevated accumulation of La in the cytoplasm of plant cells suggests that its transport across plasma membrane is metabolically mediated (Li et al., 2008).

Most of the authors, however, referred to the stimulating impact of these elements on seed germination, root growth, uptake of nutrients, nodulation and N-fixation, and on production of

chlorophyll and photosynthesis. It should be emphasized that the LAs have not been proved yet to be essential and that their biochemical functions in plants still need more study.

An ability of soybean roots to enhance the dissolution of LAs and to increase the accumulation has been reported by Nakamaru et al. (2006). The LAs accumulation in different wheat parts varies with growth stages, and at the maturity stage is in the order of roots > leaves > stems > grains (Ding et al., 2006). Fang et al. (2007) reported that main soil parameters controlling LAs bioavailability to wheat are: soil pH and amorphous Fe-oxides. Tyler and Olsson (2005) observed a lack of clear relationship between soil properties or soil LAs and leaf LAs concentration in forest-floor herbs. Variable uptake of LAs by different herb species was evident. There are evidences that both micro-organisms and earthworms increase the bioavailability of LAs (Aouad et al., 2006; Wen et al., 2006). The experiment with radiocesium indicated that mycorrhizal fungi may store Ce and limit its translocation from roots to shoots (de Boulois et al., 2008).

Wyttenbach et al.¹⁵⁵⁶ investigated the distribution of LAs in leaves of six plant species (forest trees and plants), and in pertinent soils and soil extracts. Concentrations of the individual LAs were not a function either of their total contents or their soluble forms in soils. In most cases, however, concentration ratios between species were a smooth function of the atomic number of the LAs. The plant to soil ratio for almost all LAs in needles of Norway spruce was about 5×10^{-3} but revealed large variations among individual trees. As Wyttenbach et al.¹⁵⁵⁵ concluded, these effects may be due to a change in the oxidation state (in cases of Ce) or due to differences among individual plants or plant species. Variation in LAs concentrations in needles and leaves of trees is significant: pseudoplatanus leaves contain more LAs (by about a factor of 10) than spruce needles. Also, organic complexes of the LAs in soils are believed to control plant uptake. The concentrations of each LAs and of Sc increase significantly and linearly with the needle age class. No retranslocation of the accumulated elements in spruce needles was observed.

The concentration of LAs in food plants is of special concern. Especially edible mushrooms are recently studied as accumulators of aerial pollutants (Table 8.8). The LAs contents in vegetable highly vary, and La in particular (Table 8.9). Soil dressing with these elements has variable effect

TABLE 8.8
Lanthanides in Wild Edible Mushrooms from Northern Poland^a (μg/kg)

Element	King Boletus (<i>Boletus edulis</i>)	Other Edible Mushrooms
	Mean	Range
La	27	5.3–70
Ce	56	9.3–160
Pr	6.5	1.7–58
Nd	23	6.7–67
Sm	7.3	12–14
Eu	1.9	0.7–2.2
Gd	8.1	1.4–9.5
Tb	1.3	0.8–1.6
Dy	3.7	1.1–9.9
Ho	1.5	0.7–1.6
Er	2.9	0.7–4.5
Tm	0.9	0.7–0.9
Yb	2.2	0.7–3.4
Lu	—	0.7–1.2

^a After Falandysz J., et al., 2001. *Food Add. Contam.* 18:503–513.

on their content in wheat grains, but in general increases their concentrations (Liang et al., 2005). Thus, wheat grains from China contain higher amounts of all LAs than grains from Sweden (Table 8.9). Liu¹⁰⁶⁷ found the sum of LAs contents of food plants (edible parts) to be in (mg/kg): tomato 0.05; corn 0.2; rice 0.6; wheat 1.0; and sesame 3.6. Cabbages from the background area of Denmark contain, on average, La, Ce, Pr, Nd, and Gd within the range of 0.15–2.6 µg/kg (FW), while concentrations of Sm, Tb, Dy, Ho, Er, Tm, Yb, and Lu in sprouts ranged from 0.005 to 0.06 µg/kg FW (Bibak et al. *vide* Goering, 2004).

There is no clear evidence on toxic effects of LAs to plants, however, they have impaired impact on cell membranes of vascular plants and on the Ca metabolism in microorganisms. Qiu et al. (2005) reported that LAs may regulate the biological functions of some biomolecules, however, their overdose shows an inhibitory effect on living organisms. The open questions are effects of the bioaccumulation of LAs and a long-period impact on organisms. Although LAs are known to be toxic to cell metabolism, there are some LAs (La, Pr, Nd, Eu, and Tb) that inhibit, specifically and competitively, Ca accumulation by mitochondria of microorganism cells. On the contrary, Shi et al. (2006) observed that La increases the accumulation of several elements (e.g., Se, Co, Rb, V) in chloroplast of cucumber, affecting the photosystem of leaves.

IV ACTINIDES

A INTRODUCTION

The actinides (ACs) is the term proposed for the elements from Ac through U (and Lr). The IUPAC recommended the term actinoid (An). Among the ACs only four elements: Ac, Th, Pa, and U occur naturally in the terrestrial environment, and only two elements exist in relatively large quantity as long-lived nuclides; two isotopes of U (²³⁸U and ²³⁵U) and one of Th (²³²Th). The U-series radioactive daughter, ²³⁰Th has a half-life of 75,000 years. Other ACs also have been found to occur as results of natural nuclear reactions of U, but in very negligible traces. These are mainly Ac and Pa, of which some isotopes have a relatively long half-life. The ACs have variable oxidation states, from +2 to +6 in most geological environments (Table 8.10).

Distribution and behavior of Th and U has received most attention, as the most abundant ACs in the terrestrial environments. Igneous rocks and argillaceous sediments contain usually increased amounts (Table 8.11). Geochemically, U and Th are coherent. They may substitute the LAs in some minerals and are associated with apatite and sphene. The common carriers of Th are monazite and cheralite—Ce minerals. Th also has its own minerals, for example, thorite, ThSiO₄ and thiorite, ThO₂, and can be associated with several other minerals. A major commercial ore of U is uraninite and pitchblende, of similar composition: UO₂ + UO₃.

The mobility of Th and U during weathering processes depends highly on the host minerals. When these elements become mobilized, they are very likely to be quickly precipitated as hydrolysates or absorbed and form organic complexes and various stable compounds such as oxides, carbonates, phosphates, vanates, and arsenates. The ACs easily form strong complexes with oxygen ligands, and thus their species with inorganic ligands such as OH⁻, CO₃²⁻, and HPO₄²⁻ are likely to occur in various environmental conditions. Thus, the distribution of Th and U in the lithosphere is highly controlled by the Eh–pH system.

ACs, and especially U, exhibit an affinity to be absorbed by organic matter and accumulated by microorganisms. Letunova and Kovalskiy¹⁰⁶¹ calculated the factor of bioaccumulation of U by microorganisms at 300 times as compared with its content in soils. Due to an easy U sorption by OM, its significant accumulation in coal and peat is often reported. Nakashima (1992) described that naturally occurring humic substances such as coals may play an important role in the U concentrations at various stages of sedimentary cycles. Average contents of Th and U in coal is estimated as 5.6 and 6.1 mg/kg. The environmental risk around various U mines have been recently broadly investigated (Hafenburg et al., 2007; Pereira et al., 2008; Zivotic et al., 2008).

TABLE 8.9
Lanthanides (average and range) in Vegetables and Wheat ($\mu\text{g/kg}$)

Element	Vegetables ^a	Wheat Shoots ^b	Wheat Grain ^c	Wheat Grain ^d
La	0.4–2000	155	1.7	16.8
Ce	2–50	265	3.4	26.9
Pr	1–2	30	0.4	1.9
Nd	10	121	0.9	6.8
Sm	0.2–100	20	0.2	1.1
Eu	0.04–70	<10*	<0.1	0.3
Gd	<2	21	0.2	0.2
Tb	0.1–1	<8*	<0.1	0.1
Dy	—	15	0.1	0.7
Ho	0.06–0.1	<8*	<0.1	0.1
Er	0.5–2	8	<0.1	1.8
Tm	0.2–4	<2*	<0.1	1.8
Yb	0.08–20	8	<0.1	1.5
Lu	0.01–60	<2*	<0.1	1.5

* One determination only.

^a After Laul, J. C., Weimer, W. C., and Rancitelli, L. A., *Origin and Distribution of the Elements*, Vol. 11, Ahrens, Pergamon Press, Oxford, 1979, 819.462 and Montford, M. A., et al., *Trace Subst. in Environ. Health*, Vol. 14, University of Missouri, Columbia, MO, 1980, 155.⁵⁴⁷

^b After Li F., Shang X., Zhang S. 2001. *Commun. Soil Sci. Plant Anal.* 32:2577–2587.

^c After Eriksson J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm.

^d After Liang T., Zhang S., Wang L. et al. 2005. *Environ. Geochem. Health* 27:301–311.

Among the ACs series, beside Th and U, only Pa occurs as natural unstable isotope. Other transuranic elements are artificial isotopes that resulted from Th and U decay reactions.

Americium is a man-made radioactive element that contains four principal isotopes of relatively long half-lives from 141 to 7370 years, and has no stable isotopes. The only commercially important one is ²⁴¹Am and may be found already, at very low levels, in all environmental media, as a result of fallout over the past atmospheric nuclear weapons tests and nuclear accidents (Misral, 2008).

TABLE 8.10
Selected Properties of Naturally Occurring Actinides

Element	Element	Atomic Number	Atomic Mass	Ionic radius (pm)	Oxidation state ^a	Density (g/cm ³)
Ac	actinium	89	227	126	+3	10.07
Th	thorium	90	232	108–134 ^b	+2, +3, +4	11.72
Pa	protactinium	91	231	92–109 ^b	+3, +4, +5	15.37
U	uranium	92	238	59–100 ^b	+2 ^c , +6	11.95
Pu	plutonium ^d	94	242 ^e	—	+3, +4 , +5	19.84

^a Valence values in bold are for the main oxidation states.

^b Value for the highest oxidation states.

^c The valence values can vary from +2 to +6.

^d Small amounts are generated in the natural reactors (Zhang P.-Ch., Krumhansl J.L., Brady P.V. 2002. *Geochemistry of soil radionuclides*, P.V. Brady, 1–20, SSSA Special Publ. 59, Madison, WI).

^e For the most stable isotope of Pu.

TABLE 8.11
Thorium and Uranium in Rocks and Soils (mg/kg)

Elemental Compartment	Thorium	Uranium	²³⁸ U (pCi/g) ^a
Earth's crust	3.6–9.6	0.9–1.7	0.2–0.3
Igneous rocks			
Mafic	1–14	0.3–3.0	0.2; 0.3 ^b
Acid	10–23	2.5–6	1.3–1.6 ^b
Sedimentary rocks			
Argillaceous	10–12	3–4	1.0
Sandstones	2–4	0.5–0.6	<0.3–1.0
Calcareous	2–3	2.2–2.5	0.7
Soils^c			
in Europe	0.21–53.2 ^d	0.8–11.0	—
in the United States	6.1–7.6	2.3–3.7	0.6

^a Adapted from ATSDR (2000).

^b The median and mean values, respectively.

^c Data for various soil kinds.

^d Adapted from Haneklaus S., Schnug E. 2005. *Intern. Symp. Loads and Fate of Fertilizer Derived Uranium*.

There is considerable contemporary interest in studies on the behavior of other elements of the ACs, which are isotopes released from nuclear fuel power industries. This group includes various isotopes of plutonium (Pu), americium (Am), curium (Cm), and neptunium (Np), of which the long-lived and highly radiotoxic ²³⁹Pu and ²⁴¹Am are of the greatest concern. Most of the aerosols produced and discharged from nuclear facilities, as well as in nuclear bomb fallout, are composed of PuO₂, but some of the Pu may come from the evaporation of Pu(NO₃)₄.

Information on the production of Th and U is variable; some data yielded the annual world production of Th to be 700 tons in 1984 (Reimann and Caritat, 1998), and the production of U to be 35.37 kt in 2003 (WMSY, 2004).

The use of AC isotopes has been quite recent and restricted to scientific experiments and nuclear-power industries. Th is used as coating material for optical lenses and some metallic wires, and as an addition to metallic alloys. U is applied mostly in nuclear industry and also for some very sophisticated devices. Depleted U (DU) is used in the manufacture of armor-piercing ammunition for the military and its deployment has been undertaken during recent wars. Compounds of U are used in photography for toning, for special lamps, and in the leather, ceramic and wood industries, for stains and dyes. ²³⁹Pu has received much attention recently because of its use in nuclear power reactions and weapons. It has been calculated that since 1980, the world's nuclear power reactors produced more than 20 tons Pu. In addition, Pu isotopes (mainly 239 and 240, half-life 24,000 and 6537 years, respectively) are produced for military programs (ATSDR, 2002). Elevated concentrations of these radionuclides in soils, sediments, and aquatic plants along the Yenisei river (Siberia) is reported as an effect of long-term impact of the weapon plant and mining activities (Bolsunovsky and Bondareva, 2007). Soils in the vicinity of Tomsk-Seversk (Siberia) contain (in Bq/m²): ¹³¹+²¹⁰Pu at the range 420–5900, and ²⁴¹Am at the range 160–1220 (Gauthier-Lafaye et al., 2008).

B SOILS

Uranium and thorium contents in uncontaminated soils worldwide vary within the orders (in mg/kg) of 1.9–4.4 and 8.1–11, respectively (Tables 3.2 and 8.11). However, in soils of different countries,

contents of U and Th vary within the ranges (in mg/kg) from <0.4 to 96 and from 0.1 to 45 mg/kg, respectively (Table 8.12). The maximum content of the U in European soils is given as 56 mg/kg (Haneklaus and Schnug, 2005). Apparently, large amounts of Th and U are introduced into the biosphere from fossil-fuel power plants and also from P fertilizer works.

The extensive studies carried out in the United States show relatively small variations in the concentrations of U and Th among soil types, with the exception of the radionuclides ^{238}U and ^{232}Th which are likely to be concentrated in the soils close to aquatic systems (Meriwether et al.¹⁰⁹⁰). Variable parameters (pH and Eh) of ground water may control the adsorptive reactivity of U species. The hydroxides of Th^{4+} are the dominant species in soil and in aquatic systems, although carbonate complexes are also formed (Zhang et al., 2002).

Soils of the lowland of Poland contain average amounts of Th at the value of 3.23 mg/kg, and U at the mean value of 1.6 mg/kg. In the mountain soils (Sudety Montains), amounts of U increased up to >10 mg/kg (Strzelecki et al.¹⁵⁰⁹). Surficial sediments of Finland contain, most commonly, Th in the range of 5–20 mg/kg and U in the range of 1–5.5 mg/kg (Köljonen, 1992). Yoshida and Muramatsu¹⁵⁶³ reported the lowest contents of both elements for sand dunes and peat soils of Japan (Th, 0.3 and U, 0.6 mg/kg) and the highest for red and gray lowland soils (Th, 1.4 and U, 2.9 mg/kg). In agricultural soils of Japan, median concentrations of U vary from 1.4 to 2.4 mg/kg, in Gleysols and Acrisols, respectively (Takeda et al., 2004). Swedish arable soils contain U in the range from 1.3 to 16 mg/kg, at an average value of 4.4 mg/kg (Eriksson, 2001).

Harmsen and de Haan³⁰⁶ reviewed the behavior of Th and U in the soil environment and pointed out that the formation of hydrated cations of U_2^{2+} and of Th^{4+} are responsible for the solubility of these metals over a broad range of soil pH. Also, SOM and several organic acids may increase the solubility of Th and U in soils. The mobility of Th and U in soils may be limited due to both the formation of slightly soluble precipitates (e.g., phosphates, oxides) and adsorption on clays, some minerals, and also fractions of SOM. Humic substances, and HA in particular, have an important role in the speciation of Pu due to complexing, redox, and sorption (Blinova et al., 2007). Both, HA and FA have an impact on the Th sorption by soil nanoparticles of TiO_2 , however at lower pH

TABLE 8.12
Thorium and Uranium Contents of Surface Soils of Different Countries (mg/kg)

Country	Th		U		Ref.
	Range	Mean	Range	Mean	
Reference soils					
China	8–27	—	—	—	1313
United States	3.8–12.4	—	—	—	558
Bulgaria	3.6–17.8	9.3	—	—	1065
Brazil	76; 96 ^a	—	—	—	409
Canada	4.2–14.1	8.0	0.72–2.05	1.22	818
Great Britain	—	10.5	—	2.60	235, 688
Germany	0.4–15.0	8.0	0.42–11.02	—	276
India	—	—	—	11.00	946
Italy	—	—	1.5–8	3.17	355
Poland	1.4–7.2	3.4	0.10–2.33	0.79	462, 706
U.S.	2.2–21.0	7.6	0.30–10.70	3.70	1012
U.S. (Alaska)	<1.6–76	6.1	<0.22–45	2.3	1181
Russia	—	13.4	—	3.8	

^a Two single analyses of soils near LAs ore body.

(pH <4) FA contributes more to this sorption (Tan et al., 2007). Strong organic ligands associated with microbial siderophore reveal a great adsorption capacity for UO_2 under reducing condition and might be considered for a nuclear waste storage and remediation (Frazier et al., 2005). Wolff-Boenisch and Traina (2007) reported that the siderophore effect on the desorption of U is controlled by several other factors, for example, aqueous speciation. There are several studies that show U to likely precipitate at the surface of some minerals, such as feldspars, kaolinite, goethite. Chardon et al. (2008) reported that U may form its own mineral, becquerelite, in an association with feldspar and that this process is controlled by the pH of the media.

The affinity of clay soil fraction to adsorb Th and U is shown in Figure 7.2. The addition of hydroapatite, $\text{Ca}_3(\text{PO}_4)_3\text{OH}$, to the U-contaminated sediments or soils immobilizes U due to the fixation in secondary Al/Fe phosphate phases.¹²⁰⁴ Megumi and Mamuro⁵²⁹ explained that the observed conspicuous enrichment of ^{230}Th in soil particles is the result of a higher solubility and thus a higher leaching of uranyl ions, U_2^{2+} , than of Th^{4+} ions during soil-forming processes. Meriwether et al.^{1090a} reported that in soils of Louisiana, both radionuclides ^{238}U daughters and ^{232}Th daughters are correlated with soil suborders, suggesting that the process of fractionation leads to their increase in the soils of water environments.

Spezzano and Silvestri¹¹⁵² have applied a procedure for the radiochemical determination of α -emitting nuclides of Th and U in soils. The average abundance of these isotopes in two surface soils (close to the U mills) in Italy was as follows (in Bq/kg): ^{230}Th , 52.9; ^{232}Th , 40.1; ^{234}U , 53.9; ^{235}U , 2.5; and ^{238}U , 53.7. Fertilizers are a source of ACs, and in particular the U. Most commonly, about 90% of the input to agricultural soils is attributed to superphosphate fertilizers. The mean U contents of P fertilizers vary within the range of 64.8–362 mg/kg and depend upon the U concentrations in phosphate rocks, which differ from 8 to 220 mg/kg being the highest in rocks mined in Brazil and Israel (Haneklaus and Schung, 2005). Takeda et al. (2006) calculated that superphosphate with U at 31 mg/kg increased U content up to 200 mg/m² of surface soils during 61 years. Haneklaus and Schung (2005) estimated that U loads of up to 61 g/ha by P fertilization will increase the U content in soils, and that it will require above 20,000 years to reduce the soil U to the baseline content through U uptake by harvest plants.

The importance of microorganisms in the geochemical cycle of U has been emphasized by Wildung and Garland,⁸⁷³ Trudinger and Swaine,⁸⁰⁹ and Letunova and Kovalskiy.¹⁰⁶¹ They reported that microorganisms have a great capability to accumulate U in their tissues, and the bioconcentration factor for U was up to 300 times compared with its content in soils. A great tolerance toward U was noticed in microorganisms from U-contaminated soil (Joner et al., 2007). In the soil solution of rhizosphere higher U concentration was observed than in nonrhizosphere soil (Takeda et al., 2008).

Several microorganisms common in surface and subsurface soil environments have been identified that can enzymatically reduce U^{6+} to U^{4+} , under anoxic conditions. According to Shcherbina et al. (2007) humic derivatives reduce valence states of the ACs, and thus decrease their mobility. These processes, however, are controlled by several soil parameters (pH, Eh, CEC), and in particular by the presence of Fe hydroxides. On the contrary, Abdelouas and Grambow (2004) reported that soil microorganisms could enhance the retention of U^{6+} and other radionuclides via the precipitation of highly insoluble mineral phases. There is evidence that arbuscular mycorrhizal fungi (AMF) increase concentrations of U in roots of some herb plants and may have a potential role in the phytostabilization of U in soils (Chen et al., 2005). Also Landa (2003) emphasized the role of reducing bacteria in leaching of U from Uranium Mill Tailings. Tsuruta (2003) described possible accumulation of Th by bacteria (*Micrococcus luteus* and *Streptomyces levoris*) that might have a practical use. Studies on the mobility and phase formation of the DU indicate a low migration of this metal throughout the loamy clay column (Trueman et al., 2004). Grive et al. (2004) emphasized that U cycles are closely associated with Fe cycles in various environments and are also linked to the carbonates. The sorption and coprecipitation of U^{6+} by calcium carbonates and mobilization due to the reduction to U^{4+} is of great environmental importance (Koroleva and Manginin, 2004). The increased use of apatite as a soil amendment resulted in the enhanced desorption of Th in soils and

sediments. Nevertheless, Th predominates in a residual fraction of both apatite and soil amended with apatite (Kaplan and Knox, 2004). Remedial effectiveness of phosphate on the U precipitation in contaminated sediments was partly reduced by microbial activities (Knox et al., 2008).

There is presently a considerable interest in the behavior of other ACs, which are isotopes not occurring naturally but released from the nuclear fuel power industries. This group includes various isotopes of plutonium (Pu), americium (Am), curium (Cm), and neptunium (Np), of which ^{239}Pu and ^{241}Am , long-lived and highly radiotoxic, are of greatest concern.

The behavior of these radionuclides, and of ^{239}Pu in particular, was extensively reviewed by Wildung and Garland,⁸⁷³ Vyas and Mistry,⁸³² and Silver.¹¹⁴⁹ Regardless of the forms of Pu and Am entering soils, mainly from the aerosols produced and discharged by the nuclear facilities, their behavior is controlled by various soil factors. Jakubick³⁵⁰ described in detail the geochemistry of the worldwide fallout and discharge of Pu. He concluded that the behavior of PuO_2 discharged from a nuclear facility can give information about the environmental impact of the nuclear industry. Average fallout of $^{239+240}\text{Pu}$ on soils in the temperate zone of the United States, has been calculated at $7.8 \times 10^4 \text{ Bq/km}^2$ and of ^{238}Pu at $1.9 \times 10^3 \text{ Bq/km}^2$ (Hanson *vide* ATSDR, 2002). The concentration of Am in soil in the New York region has been estimated in 1969 at 2 MBq/km^2 , which may increase up to 33 MBq/km^2 in the year 2035, resulting from cumulative deposition (ATSDR, 2002). During the period 1969–1983, the mean annual fallout of Am to Antarctica was about 8.3 mBg/m^2 .

The levels of ^{238}Pu in soils of the United Kingdom were detected in the range of $0.2\text{--}18 \text{ nCi/kg}$, and of $^{239+240}\text{Pu}$ in the range of $0.8\text{--}83 \text{ nCi/kg}$ (ATSDR, 2002). Amounts of $^{239+240}\text{Pu}$ in surface layer of the contaminated soil near Heidelberg, Germany, were at $0.13\text{--}0.45 \text{ mCi/km}^2$ (Jakubick³⁵⁰). Soils of Kazakhstan sampled in 1992 contained $^{239, 240}\text{Pu}$ in the range of average values from 10 to 93 mCi/km^2 (Panin, 2004). Roussel-Debet (2005) studied the residence time of ^{241}Am and $^{239+240}\text{Pu}$ in agricultural soils and discussed the use of K_d values for better assessments of their behavior. In general, however, the rate of vertical migration of both elements is low, as it was confirmed for agricultural soils near Chernobyl (Mboulou et al. *vide* Roussel-Debet, 2005). The concentration of both Pu radionuclides (239 and 240) in surface soils of Iran, as effect of fallout pollution, is reported at the range of $80\text{--}360 \text{ mBq/kg}$ (Aliabadi et al., 2005). Soils of Belarus contained $\text{Pu}^{239+240}$, in theyear 2001, up to 190 and 780 Bq/m^2 (Entwistle et al., 2005).

In soils, Pu occurs mainly as complexes of FA and HA and in forms absorbed by fine mineral particles, often coated with organic layer. Oxide compounds, like PuO_2^{2+} , are more stable than nitric compounds, $\text{Pu}(\text{NO}_3)_4$, which are likely to occur in soil solution as hydroxides and are easily soluble, and therefore available to the plant. Relatively mobile, and thus available PuO_2 migrates slowly into deeper soil layers, but most of this compound remains within the 10 cm top-soil layer. Pu is adsorbed on hematite in larger amounts than on silica and montmorillonite (Runde, 2002). Microbial activity, as well as other soil parameters, such as low pH, low clay content, and low OM may enhance the Pu mobility.

Unlike the tightly bound PuO_2^{2+} , $\text{Pu}(\text{NO}_3)_4$ belongs to the soluble compounds, and mainly as hydroxide species is likely to be present in soil solution. Thus, the soluble, and therefore phytoavailable fraction of Pu, and apparently of other transuranic elements, appears to be largely present as particulates of hydrated oxides and as organometallic complexes. Bartlett⁹³³ reported that Pu compounds, when converted into the mobile anion forms, became more available and toxic than oxides. Jakubick³⁵⁰ studied in detail the behavior of ^{239}Pu and ^{240}Pu in meadow soil around Heidelberg, Germany, where the isotopes have been concentrated from 290 to 450 mCi/km^2 in the 10 cm-deep upper layer, whereas the activity of these isotopes ranges from 1.6 to 5.8 mCi/km^2 at a depth below 25 cm. Little et al.¹⁰⁶⁶ investigated a buffer zone near Denver, Colorado, which was contaminated with Pu between 1959 and 1964. They found that the top layer (21 cm) of soil contained above 99% of the total Pu inventory, which averaged about 53 mCi/m^2 in the studied area. Concentrations of Pu in vegetation were relatively low, but were several orders of magnitude larger than in experimentally grown plants.

Allard et al.⁹¹⁷ studied the adsorption of ^{241}Am in the presence of humic materials and found that this radionuclide is associated to solids of organic origin or to inorganics which are coated with an

organic layer. ^{241}Am also makes humate complexes easily. At a high pH and OM content, the adsorption of this radionuclide is reduced, increasing its mobility in the environment.

To protect soils against contamination with radionuclides (U, Th, Np, Pu), they are stored in the form of glass fusion. Aqueous leaching of nuclear glass under geological disposal conditions mobilizes the elements that were precipitated (up to 98% of realized amounts) at the surface of glass. The presence of amorphous silica and phosphates stimulated these processes.¹⁴¹²

C PLANTS

The assessment of the transfer of Th, U, and transuranic radionuclides from contaminated soils to plants is important in environmental research. The soluble fractions of these elements in soils seem to be readily absorbed by plants, and this is clearly supported by the studies conducted in the U geochemical province where plants accumulated up to 100 times more U than did plants from other areas. However, Zhang et al. (2002) described that surface contamination, rather than uptake by roots, should be considered as primary source of Pu in plants. Also Yoshida and Muramatsu¹⁵⁶⁴ reported that U and Th are slightly available to all kinds of plants, including mushrooms and yielded the following ranges for these elements in forest plants (in $\mu\text{g/kg}$): for Th, 3–36 and for U, 1–12. Chang et al. (2005) observed the increased uptake of U by Indian mustard (*Brassica juncea*) when citric acid was applied, and suggested that this might be useful for the phytoextraction of U from contaminated soil. Aouad et al. (2006) reported that at the presence of bacteria (*Pseudomonas aeruginosa*) plants (corn) take up elevated amounts of both LAs and ACs. Effects of the U and Th treatments on the concentrations of both macronutrients and trace elements are variable and depend on different plants species and elements (Shtangeeva et al., 2007). The most important reaction was decrease of Ca in wheat seedlings under Th addition to the growth medium (Shtangeeva et al., 2005). Increased level of U in the nutrient solution (up to 1000 $\mu\text{mol U/L}$) can cause oxidative stress and cellular redox imbalance in plants (Vandenhove et al., 2006). Haneklaus and Schnug (2005) discussed processes of the U uptake by plants and calculated a relatively low value of the soil–plant factor—0.05. Nevertheless, increased levels of both U and Th in tree leaves grown on contaminated sites indicate their bioavailability (Table 8.13). Variable U contents of food plants reveal influence of both plant species and growth conditions (Table 8.14). Contents of U in these plants vary from <1

TABLE 8.13
Uranium and Thorium in Leaves of Trees Grown on Background and Contaminated Sites of Wetland in South Carolina, United States^a

Sample	Uranium-238 (mg/kg)		Thorium-232 (mg/kg)	
	BS	CS	BS	CS
Soil	6.7	284	1.3	166
Red Maple, <i>Acer rubrum</i> L.	bdl	0.5	0.03	2.6
Water Oak, <i>Quercus nigra</i> L.	0.0013	1.6	bdl	0.4
Sweetgum, <i>Liquidambar</i> <i>styraciflua</i> L.	0.04	8.2	0.04	5.3

BS = Background site.

CS = Contaminated site.

bdl = Below detection limit.

^a Adapted from Hinton T.G. et al. 2005. *J. Radioanal. Nucl. Chem.* 264:417–422.

TABLE 8.14
Uranium in Some Food Plants of United States^a (μg/kg FW)

Plant Food	Content
Potato, tubers	2.7–18
Potato, tubers ^b	38.9
Carrots	7.7
Cabbage	4.7
Parsley	60
Red pepper	5
Fresh fruits	0.7–1.3
Fresh vegetables	0.5–0.9
Wheat bread	19
Sunflower ^b	4.3–24.6
Wheat ^b	3.2

^a Adapted from ATSDR. 2002. *Draft toxicological profile for several trace elements*. U.S. Dept. Health & Human Services. Agency for Toxic Substances and Disease Registry, Atlanta, GA, unless otherwise indicated.

^b After Haneklaus S., Schnug E. 2005. *Intern. Symp. Loads and Fate of Fertilizer Derived Uranium*.

to 60 μg/kg (FW). According to Laul et al.⁴⁶² Th contents of vegetables range from 8 to 20 μg/kg, whereas Bowen⁹⁴ yielded much wider range for Th in land plants, from <8 to 1300 μg/kg.

Tiffin⁷⁸⁹ reported that a U-protein complex was found in leaves of *Coprosma australis* (Rubiaceae family), while the mineral precipitates (autunite, $\text{Ca}(\text{UO}_2\text{PO}_4)_2 \cdot 10\text{H}_2\text{O}$) were found in the tips of plant roots.^{1042a} Wildung and Garland⁸⁷³ stated that plants possess the ability to effectively accumulate soluble Pu and to transport the Pu from roots to shoots. However, in the area polluted with Pu, much of the Pu associated with vegetation was attached to the plant surface.⁹⁸⁰ Dienstbach et al.⁹⁸⁰ found that the proportion of the Pu isotopes (239, 240) in soils and in linden leaves showed a relative decrease of ²⁴⁰Pu in the vegetation.

Shacklette et al.⁷¹⁰ found the highest U concentration in trees on mineralized ground to be 2.2 mg/kg (AW), and Goswami et al.²⁷⁶ reported the U range from 0.5 to 4.4 mg/kg (AW) (average, 1.8) in xerophytic and mesophytic vegetation. Sagebrush grown near a P fertilizer works accumulated up to 8 mg/kg U (AW).²⁷⁸ Bowen⁹⁴ estimated the range in U concentrations in terrestrial plants to be 5–60 μg/kg, whereas Laul et al.⁴⁶² reported U concentrations in corn and potatoes to be 0.8 μg/kg.

Rühling et al.¹¹³⁵ found in mosses (mainly *Hylocomium splendens*) from the Scandinavian countries the U concentration in the range of 30–120 μg/kg, whereas Berg and Steinnes¹²²³ reported in moss samples from these countries the U contents within the range (in μg/kg) 2.8–1300 (mean 50), and Th contents in the range of 4–5100 (mean 70).

Lichens are found to be good monitors of concentrations of U in air and were used to assess the U levels in the Balkan area, after the use of DU during the conflict in 1999. The U contents of lichens varied widely depending on species and sampling sites. The highest levels, from 81 to 306 μg/kg, seem to be found in *Pseudevernia* sp. collected in Greece. According to the statements of Loppi et al. (2003) the average U concentration was in a line with the values reported in lichens from other countries and does not indicate any contamination by DU in this area.

Kierepko et al. (2008) measured the activity ratios of ²²⁸Th: ²³²Th and ²³⁰Th: ²³²Th in various environmental samples and concluded that relative increased levels of ²²⁸Th in plants (e.g., bilberry leaves, spruce needles) is from the decay of ²²⁸Ra that is more mobile and thus easier taken up by plants.

9 Elements of Group 4 (Previously Group IVb)

The trace elements of group 4 are titanium (Ti), zirconium (Zr), and hafnium (Hf). Ti is associated with silicate minerals and considered a trace element only because of its low concentrations in plant and animal tissues. The next two metals, Zr and Hf, are widely distributed in both the litho- and biosphere and are often included in the REE group. The geochemical properties and terrestrial abundance of these elements as well as the physical and chemical properties differ (Table 9.1). Their common characteristics are the weak solubility of their hydroxides and oxides in water, an affinity to bond with oxygen.

I TITANIUM

A INTRODUCTION

Titanium shows the strong lithophilic characteristic and is a common constituent of several rocks, in the range of 0.4–10%. Its average abundance in the Earth's crust is calculated as 4.4 (Table 9.2). Ti exhibits variable valences (Table 9.1), but in minerals occurs mainly in the tetravalent oxidation state, TiO_2 , as a major component of oxides, titanates, and silicates. The most important and of an economic value are: ilmenite, FeTiO_3 ; rutile, TiO_2 ; and to a lesser degree, sphene (titanite), $\text{CaTiO} \cdot \text{SiO}_4$. Anatase and brookite are also composed of TiO_2 , but have different crystallographic coordinations. Many of Ti-containing minerals are resistant to weathering and they are often associated with other heavy, resistant minerals that are accumulated in some deposits.

The annual global production of Ti (as TiO_2) in 2008 was 6,250 kt (USDI, 2009). It is obtained mainly from rutile and ilmenite deposits. Most of the mined Ti is used for the production of white pigments for various manufactures. It serves as catalyst in the production of polyethylene. It is also used in the aeronautic industry and is added to metal plates, pins, etc. Additional, but significant use of Ti is in alloys, especially for orthopedic implants and prosthesis. Titanium dioxide is applied in cosmetics, mainly in the therapy of skin disorders. It is an additive to food and toothpaste and is used in variety of tablet-coating formulations.

B SOILS

The Ti content in soils vary highly from 0.01% to 2.5%, being the lowest in histosols (Table 9.2). Soils exposed to effluents or emissions from certain industries (Ti alloys, Ti paint production) may become contaminated by Ti, however, this element does not create any environmental problems.

Minerals of Ti are very resistant to weathering; therefore, they occur practically undecomposed in soils. When Ti-bearing silicates are dissolved, the element is soon transformed into the Ti oxide-aquate, which is transformed to anatase or rutile. Bain^{41a} reported that Ti in Podzols developed on glacial drift is almost entirely in the form of cryptocrystalline anatase. Hutton,³³⁴ however, stated that Ti can enter into the structure of some layered silicates. Hiller et al.¹⁰²⁵ described Fe–Mn concretions of surface marsh soils containing up to 39% of Ti. Apparently, under reducing conditions, Fe^{2+} ions are adsorbed on surfaces of Ti minerals and, followed by the oxidation to Fe^{3+} , may lead to the formation of pseudorutile.

TABLE 9.1
Selected Properties of Trace Elements of Group 4

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C, g/cm ³)	Valence ^b
Ti, titanium	22	47.87	200	4.5	+2, +3, +4
Zr, zirconium	40	91.22	216	6.5	+2, +3, +4
Hf, hafnium	72	178.5	216	13.3	+4

^a Approximately average values for the main oxidation states.

^b Values in bold are for the main oxidation state.

Although Ti minerals are known to be the most stable minerals in the soil environment, no mineral is completely insoluble, and the Ti level reported in soil solutions is 0.03 mg/L.³³⁴ When Ti-bearing silicates are dissolved, the metal is soon transformed into Ti oxide-aquate and transformed to anatase or rutile. Anatase seems to be the most abundant Ti-mineral in soils. However, Ti can enter into the structure of some layered silicates and is likely to be absorbed on surface of Fe–Mn concretions.

The solubility of Ti in soils is, very limited and this affects an increase in relatively stable amounts of Ti in the top horizon of soils, after the loss of some clay-size layered silicates due to weathering. The total Ti (also Zr) contents of soil have been used in several studies of soil genesis and of the continuity of soil profiles.

C PLANTS

Contents of Ti in plants seem to be highly controlled by soil properties and origin. Anke and Seifert (2004) presented the variation in Ti mean contents in various plants as affected by geological origin

TABLE 9.2
Abundance^a of Titanium, Zirconium, and Hafnium in Rocks and Soils (mg/kg)^a

Rock/Soil	Ti ^a	Zr	Hf
Earth's crust	0.4–0.57	100–200	3–4.9
Igneous rocks	—	—	—
Mafic	0.3–2.4	80–200	1–4.8
Acid	0.3–3.4	140–240	4.5–5
Sedimentary rocks	—	—	—
Argillaceous	0.6–2.7	160–200	2.8–6
Sandstones	0.15–3.6	180–250	3–6
Calcareous	0.4–4	20	0.3–0.4
Soils ^b	0.33	300	3
Arenosols (sandy)	0.02–1.7	90–200	1.8–18.7
Podzols (medium loamy)	0.5–1	200–550	20.8
Cambisols (heavy loamy)	0.1–2.4	330–850	—
Calcisols (calcareous)	0.04–1	—	—
Histosols (organic)	0.01–0.5	32	0.0X–0.X ^c

^a Values for Ti are in %.

^b Soil groups are given according to the WBR (Table 3.1).

^c The order of magnitude. (Data from Markert, B. and Lieth, H., Element concentration cadasters in a Swedish biotope. *Fresenius Z. Anal. Chem.*, 327, 716, 1987.)

of soils. The highest contents of Ti, at about 100 mg/kg, were found in plants from loess and some weathered *in situ* soils, whereas the lowest concentrations were in plants grown on Histosols.

Titanium in food plants ranges from 0.13 to 6.7 mg/kg. The lowest values are in prepared cereals and fruits (apples, bananas, and oranges) and the highest in lettuce, radish, and corn. Contents of Ti in grain crops from Kazakhstan range from 1.2 to 7 mg/kg and in wheat flour, from 0.4 to 1.0 mg/kg FW (Grabarov, 1970). In Swedish cereal grains, mean Ti concentrations are 0.17 and 0.25 in wheat and barley, respectively (Eriksson, 2001). The concentration of Ti in plants decrease with age and may be reduced by one-third in older plants as compared with plants in early growth stage (Anke and Seifert, 2004). Some weeds, especially horsetail and nettle are known to accumulate more Ti, up to 80 mg/kg. The phytoavailability of Ti is low; the TF values are calculated for grass pasture as 0.03–0.04 (Vera Tome et al., 2003).

No clear evidence of a biochemical role of Ti has been given, although there are some suggestions on possible catalytic function in the N fixation by symbiotic microorganisms and in the photooxidation of N compounds by higher plants (Pais and Jones¹⁴⁴⁸). These authors described some beneficial effects of Ti-chelates (mainly ascorbates) on the photosynthesis and on the molecular N₂ fixation. Also Simon et al.¹⁴⁹⁵ reported that the addition of Ti stimulates the growth of rhizobium bacteria strains. Only one early report by Wallace et al.⁸⁴¹ has described Ti toxicity symptoms at the content of 200 mg/kg in bush bean, as necrotic and chlorotic spots on leaves.

Although little attention has been given to the Ti absorption by plants, this element is considered to be relatively unavailable to plants and not readily mobile in them. Ti is still far from being accepted as an essential element to plants,¹¹⁸⁴ but there are some reports of its beneficial effects on yield of several crops.^{1113a}

Levels of Ti in plants vary rather considerably within the range of 0.15–80 mg/kg (Table 9.3). Some weeds, especially horsetail and nettle, are known to accumulate much more Ti, and diatoms are reported to contain Ti concentrations ranging from 15 to 1500 mg/kg.⁸⁵⁵

Concentrations of Ti in moss from Norway average 53 mg/kg and range from 12 to 310 mg/kg (Berg and Steinnes¹²²³). Apparently, lichens and mosses can be bioindicators for Ti aerial pollution.

TABLE 9.3
Mean Titanium Contents of Plant Foodstuffs (mg/kg)

Plant	Tissue Sample	FW Basis (574)	DW Basis (197, 267, 705)	AW Basis (145, 705)
Wheat	Grain	—	0.9	—
Corn	Grain	—	2.0	<5–20
Asparagus	Stem	—	—	180
Snap bean	Pods	—	3.2	45
Bean	Pods	<0.2	—	—
Lettuce	Leaves	<0.3	—	—
Cabbage	Leaves	<0.7	—	—
Carrot	Roots	<0.5	—	<5
Potato	Tubers	—	—	18
Onion	Bulbs	—	1.6	37
Cucumber	Fruit	<0.5	—	19
Apple	Fruit	<0.004	0.18	10
Orange	Fruit	<0.1	0.15	4
Food plants	Edible parts	—	0.2–80	—

Note: References are given within parentheses.

II ZIRCONIUM

A INTRODUCTION

The crustal abundance of Zr varies from 100 to 200 mg/kg, being the lowest in ultramafic rocks and calcareous sediments (Table 9.2). Zirconium exhibits both oxyphilic and lithophilic tendencies and its predominant valency is +4 (Table 9.1). Its main mineral is zircon, ZrSiO_4 , but baddeleyite (zirconia), ZrO_2 , has also technological importance. It occurs in several complex silicates and is associated with Ti and Hf minerals.

Zirconium is obtained as sand deposits which are most often enriched in U and Th what leads to environmental concern. Its production in 2008 was estimated at 1.36 Mt (USDI, 2009). It is also obtained as a by-product of the Ti production.

The principal use of Zr is for atomic energy purposes. Due to its great resistance to heat (melting point 4377°C) and to corrosion, it is an important component of alloys. Zirconia is used in glass, ceramics, and various thermal installations. It is also applied for water-repellent textiles, dyes, and pigments; and utilized in pyrotechnics. Some Zr minerals (zircon and baddeleyite) are used for the gem zircons as a substitute for diamond, in different colors, for jewelry.

The important application of Zr-metal is in medicine as an addition to implant materials for bones and muscles. ZrO_2 is also added to bone cement for better X-ray contrast (Schaller, 2004). This metal is a component of some cosmetics and toothpaste.

B SOILS

The Zr content of soils generally is inherited from parent rocks; therefore, no significant variation in the Zr content is observed among the soil types. Lower amounts of Zr are in soils on glacial drift (70–200; mean, 140 mg/kg) and higher amounts are in residual soils derived from Zr-rich rocks (70–200; mean, 305 mg/kg). Increased Zr contents in coarse fractions of desert dust confirmed its association with detrital zircon (Castillo et al., 2008).

The average Zr content calculated for various soils of the United States is 224 mg/kg, while Hutton³³⁴ gave the average of about 350 mg/kg Zr for Australian soils. Wells⁸⁶¹ found Zr in soils derived from basalts and andesites to range from 330 to 850 mg/kg and Lukashev and Pietukhova⁴⁹³ gave the range of Zr for sandy soils as 90–160 mg/kg and for peat soil as little as 32 mg/kg. Waganov and Nizharadze¹⁸¹ reported the mean Zr content of deep loess deposit in European Russia to be 470 mg/kg, and Protasova and Kopayeva¹¹²³ found Zr in Russian chernozems to range from 200 to 550 mg/kg. There is no observed difference in Zr contents, ranging from 100 to 550 mg/kg in both urban and industrial soils from Argentina (Custo et al., 2002). Govindaraju¹³¹³ reported that Zr contents in reference soils from China range from 219 to 500 mg/kg (mean, 281 mg/kg), and in soils from the United States range from 184 to 760 mg/kg (mean, 279 mg/kg). Chattopadhyay and Jervis¹³² reported the range of Zr in garden soils to be 200–278 mg/kg.

Organic acids seem to be the transporting agents for the migration of Zr in soils. Smith and Carson⁷⁴¹ reported that small mobility of Zr have been noted in both acidic podzolic soils and in alkaline laterites. Ferrand et al. (2006) observed a higher mobility of Zr in acid soils and its strong retention on SOM, and partly on Mn oxides.

Similar to Ti, Zr has been used as an index element in soil studies. Hutton³³⁴ extensively reviewed this topic and concluded that reliable results for soil genesis are obtained when Ti to Zr ratios are considered. Zr migration may serve as an indicator of a biogeochemical cycle balance for large ecosystems.⁷⁴¹

C PLANTS

Smith and Carson⁷⁴¹ reviewed the history of studies of stable Zr and ^{95}Zr in plants and showed that concentration factors for Zr derived from soil are low in plants, while those derived from rainwater

are much higher for both soil-rooted plants and epiphytes. This explains the relatively high content of Zr in Norwegian moss (*Hylocomium splendens*), ranging from 0.06 to 12 mg/kg (mean, 0.35 mg/kg) what indicates its source from dust and rainwater (Berg and Steinnes¹²²³). Bowen⁹⁴ gave the range in Zr concentrations in lichens and bryophytes as 10–20 mg/kg. The ready uptake of atmospheric ⁹⁵Zr by terrestrial plants due to deposition of fallout particulates is reported to contribute a great proportion of this radionuclide in the Japanese diet.⁷⁴¹

Although most soils contain relatively significant amounts of Zr, its availability to plants, presumably in anionic form, $\text{Zr}(\text{OH})_5^-$, is greatly limited. The Zr contents seem to be higher in roots, especially in nodules and roots of legumes, than in the upper parts, which apparently indicate a low mobility of this metal in plants.²⁸³ The TF average value for the accumulation of Zr by grass pasture calculated as 0.09 clearly confirmed its low phytoavailability (Vera Tome et al., 2003). Ferrand et al. (2006) studied the phytoavailability and behavior of Zr in soils. The authors confirmed the Zr accumulation mainly in roots of plants, for example, on control soil, tomato plants contain (mg/kg) Zr at levels 0.56 and 7.96, in aerial parts and roots, respectively. TF values for Zr decreases, depending on forms of Zr added to soil, in the following sequence: $\text{Zr-acetate} > \text{ZrOCl}_2 > \text{Zr}(\text{OH})_4 \sim \text{natural Zr forms}$. It has been observed that different sources of Zr (chemical forms), and especially Zr with organic ligands highly control its uptake by plants.

There is not much agreement among the reported values for Zr in plants (presumably due to low reliability of analytical results), however there is no accumulation of this metal in food plants. The Zr levels in food plants vary from 0.005 to 2.6 mg/kg, being the lowest in cereals and the highest in peanuts and beans (Table 9.4). Winter wheat and barley grains grown in Sweden contain Zr at the mean value of 0.008 and 0.013 mg/kg, respectively (Eriksson, 2001). Some herbage, especially legumes, trees, and shrubs are likely to concentrate more Zr than other plants. Herb plants sampled in 1999 along highways in Germany contained Zr in the range of 0.07–0.92 mg/kg, being the highest in dandelion (Djingova et al., 2003).

Although toxic effects of Zr on plants, especially on root growth, are commonly reported, its stimulating effect on the growth of yeasts and on metabolism of other microorganisms has also been observed.⁷⁴¹

TABLE 9.4
Zirconium Content of Plant Foodstuffs (mg/kg)

Plant	Tissue Sample	FW Basis (574, 741)	DW Basis (197, 705, 741)	AW Basis (705, 741)
Cereal	Grains	0.08–10	0.02–1	8–1033
Corn	Grains	—	—	<20
Bean	Pods	<0.13	2.6	—
Lettuce	Leaves	0.41–0.62	0.56	4
Cabbage	Leaves	<0.4	—	<20
Carrot	Roots	<0.32	—	<20
Potato	Tubers	—	0.5	12
Onion	Bulbs	0.45–0.84	—	<20
Tomato	Fruits	0–1.79	—	<20
Apple	Fruits	0.31	—	<20
Orange	Fruits	0.05	—	<20
Grape	Raisins	—	1.5	—
Peanuts	Seed	—	2.3	—
Food plants	Edible parts	—	0.005–0.2	—

Note: References are given within parentheses.

Davis et al.¹⁷¹ reported Zr to be the least toxic element, among metals, to barley seedlings. Pais and Jones¹⁴⁴⁸ described that Zr treatment enhances protein synthesis and changes the amino acid composition of proteins of some microfungi, but also reduces the availability of phosphates to phytoplanktons.

III HAFNIUM

A INTRODUCTION

Crystallographic and chemical properties of Hf are very analogous to those of Zr, especially resemblance of the atomic radius is remarkable (Table 9.1). However, its terrestrial abundance is much lower than Zr and ranges between 3 and 5 mg/kg. A bit higher Hf contents, up to 6 mg/kg can be found in sandstone (Table 9.2).

Hafnium occurs mainly in minerals of Zr, such as zircon, $(\text{Zr,Hf})\text{SiO}_4$ and baddeleyite, $(\text{Zr,Hf,Ti,Fe,Th})\text{O}_2$, and may also be associated with other minerals such as biotite and pyroxenes.

The global annual production of Hf in 1997 was estimated at about 60 t.¹³⁵⁷ Hf is used mainly (up to 90% of its production) in the nuclear industry, to make superalloys, especially for reactor control rods and coatings for cutting tools. It is applied in photographic flashes. Also biomaterials can contain Hf due to its good biocompatibility and osteoconductivity (Szilágyi, 2004).

B SOILS

The worldwide average Hf content of soils is estimated at 6.4 mg/kg, within the range of 2.5–12.7 mg/kg (Table 3.2). Contents of Hf in mineral soils are reported to range between 2 and 20 mg/kg, whereas in Histosols its concentration is much smaller (Table 9.2). Increased levels of Hf in coarse fractions of desert dusts suggest its association with detrital fraction (Castillo et al., 2008).

Reference soils from China contain Hf from 7 to 14 mg/kg (mean 7.9), and soils of the United States contain from 2.5 to 17 mg/kg (mean 7.3) (Govindaraju¹³¹³). The median Hf content of the worldwide soils is 5 mg/kg, with a range of 1–10 mg/kg.

The Hf content of soils is reported to range/average (in mg/kg) as follows: (1) Bulgaria,⁵⁵⁸ 1.8–18.7; (2) Canada,⁴⁰⁹ 1.8–10; (3) United Kingdom,⁸¹⁸ average 5; (4) EU Russia,¹¹⁸¹ average 20.8; and (5) Sweden (Eriksson, 2001), average 7.6.

C PLANTS

The common range of Hf in plants was given as 0.01–0.4 mg/kg. Some parts of plants, for example, spruce bark, contain a bit higher amounts of Hf, up to 11 mg/kg (Reimann and de Caritat, 1998). Lieth and Markert¹⁰⁶³ reported Hf content of blueberry tops to be <1 mg/kg. Eriksson (2001) found the Hf concentrations in cereal grains to be at the mean values of 0.4 and of 0.6 $\mu\text{g/kg}$ for wheat and barley, respectively. Food plants contain Hf within the range of 0.6–1.1 $\mu\text{g/kg}$ FW, but it was not always detectable (Oaks et al.⁵⁷⁴). Although Hf is very slightly available to plants, its elevated contents, in plants grown on soil amended with sewage sludge were observed. As reported by Furr et al.,²⁵⁰ Hf contents of those plants average about 3 mg/kg.

10 Elements of Group 5 (Previously Group Vb)

Geochemical characteristics of the metals of group 5, vanadium (V), niobium (Nb), and tantalum (Ta), are variable, although all elements exhibit mainly lithophilic tendencies. Vanadium is widely distributed in terrestrial environments where it forms both cationic and anionic compounds. Two elements, Nb and Ta, have very similar atomic radius and resemble each other in geochemical properties (Table 10.1). Both metals are rather rare in the biosphere (Table 10.2), are highly associated with Fe, Ti, Mn, and Zr, and are likely to be concentrated in polymetallic concretions in the ocean bottom. All metals of this group reveal an affinity for oxygen bonds.

I VANADIUM

A INTRODUCTION

The abundance pattern of V in rocks shows its tendency to be concentrated in mafic igneous rocks, up to 130 mg/kg, and in argillaceous sedimentary rocks, up to 250 mg/kg (Table 10.2). Geochemical characteristics of V are strongly dependent on its oxidation state (Table 10.1) and on the acidity of media. Under weathering conditions V^{5+} predominates. At this oxidation state, V shows isomorphic relation to other cations, such as As^{5+} and Mo^{5+} , whereas V^{2+} behaves similarly to Fe^{2+} .

Vanadium does not form many own minerals, of which the most important are vanadinite, $Pb_3Cl(VO_4)_3$; roscoelite, $KV_2(OH)_2(AlSi_3O_{10})$; mottramite, $Pb(Cu,Zn)(VO_4)(OH)$; and patronite, of variable composition: VS_2 , VS_4 , and V_2S_5 . V can form variable compounds (V-oxysalts), of which $(VO_4)^{3-}$ plays a significant role due to adsorptive properties, such as carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$. V occurs commonly as an admixture in about 70 minerals. Most of the V-containing minerals, however, are of secondary origin. V is very often associated with primary minerals such as pyroxenes, hornblende, biotite, and magnetite. During weathering, the mobility of V is dependent on the host minerals and on pH-Eh conditions, and is finely incorporated into clay minerals, and Fe-hydroxides. Some V-ions, for example, $(VO_4)^{3-}$, are easily fixed to the surface of clay particles and often together with phosphates to secondary apatites.

Vanadium reveals lithophilic affinity, and also is highly concentrated in several bituminous sediments and coals. Its average content in coal is estimated at 58 mg/kg, and in fly ash at 208 mg/kg (Llorens et al., 2000). However, some elevated concentrations of V are reported (in mg/kg) in (1) fly ash up to >1000, (2) crude oil up to 900, (3) crude-oil ash up to 22,000, and (4) asphalt, up to 6000.¹³⁵⁷ Wedepohl⁸⁵⁵ explained these phenomena, following the assumption of Bertrand, by postulating that in the former geologic periods there might have existed some plants with much higher V content than presently found in normal plants. Yeh⁸⁹⁴ described high concentrations of V in organic sediments as the results of V^{3+} sorption by lipids and cholines, the basic compounds in further formation of porphyrins. A possible diadochous substitution of Mg^{2+} by vanadyl ions VO^{2+} is another explanation for the high amounts of V in some porphyrins.¹¹²⁰

Global production of V in 2008 was 60 kt (USDI, 2009). Some quantities of V are recovered from petroleum residues, ashes, and catalysts (ATSDR, 2002).

Various compounds of metallic V are currently used for a wide variety of purposes. A great proportion of this metal (about 85% of mined metal) is utilized as an agent in the steel industry, mainly

TABLE 10. 1
Selected Properties of Trace Elements of Group 5

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C, g/cm ³)	Valence ^b
V, vanadium	23	50.9	192	6.1	+2, +3, +4, +5
Nb, niobium	41	92.9	208	8.6	+2, +3, +4, +5
Ta, tantalum	73	180.9	209	16.7	+3, +4, +5

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation states.

for heat-resistant and high-strength alloys, especially for high-speed tools (in vibration). It is a component of alloys in the manufacture of jet aircraft engines. It is a significant corrosion inhibitor.

Small quantities of V play an important role as a catalyst in the production of some chemicals, glass, ceramic, and also in electronic industries. Some dyes for textiles contain V compounds. It is also added to some pesticides and is applied as a photographic developer.

B SOILS

Levels of V in soils are closely related to the parent rock types. Its worldwide soil average is estimated at 129 mg/kg, within the range of 69–320 mg/kg (Table 3.2). V is distributed in soil profiles rather uniformly and the variation in V content of soil is inherited from the parent materials. Thus, the highest concentrations of V (up to 500 mg/kg) are reported for Cambisols, often soils derived from mafic rocks (Table 10.2). The lowest V contents (up to 150 mg/kg) were found in peat soils

TABLE 10.2
Abundance of V, Nb and Ta in Rocks and Soils (mg/kg)

Rock/Soil	V	Nb	Ta
Earth's crust	35–60	26	1.5–2.2
Igneous rocks	—	—	—
Mafic	40–250	10–35	0.5–2
Acid	40–90	15–60	2–4
Sedimentary rocks	—	—	—
Argillaceous	80–130	15–20	0.8–1.7
Sandstones	10–60	0.5–10	0.5–1.5
Calcareous	10–45	0.05–0.1	0.01–0.05
Soils ^a	—	—	—
Arenosols (sandy)	10–220	12.5 ^b	1.1–2.7 ^d
Podzols (medium loamy)	20–330	4–44 ^c	0.4–3.9 ^e
Cambisols (heavy loamy)	20–500	30–300	0.17–0.22 ^f
Calcisols (calcareous)	—	—	—
Histosols (organic)	30–150	—	—

^a Soil groups are given according to the WBR (Table 3.1).

^b Mean for various soil of Lithuania.¹³⁵⁹

^c Mean for various soils of the United States.⁷⁰⁷

^d Range for soils of the United States.⁴⁶²

^e Range for soils of Bulgaria.⁵⁵⁸

^f Range for garden soils of Canada.¹³²

(Histosols). Surface horizons of some Podzols are reported to contain relatively small amounts of V as a result of extensive leaching into lower horizons.⁷¹

The reference soils of the United States contain V in the range of 36–150 mg/kg (Govindaraju¹³¹³). Fairly uniform contents of V, presented as average values from 79 to 91 mg/kg, are reported for various soils from different regions of Russia (Protasova and Kopayeva¹¹²³). Geometric mean of V in representative soils of Poland is 18.4 mg/kg (Dudka and Markert, 1992). Agricultural soils from Sweden contain V within the range of 28–111 mg/kg, at an average value of 69 mg/kg (Eriksson, 2001). The median V contents in agricultural soils of Japan vary from 94 mg/kg in Gleysols to 250 mg/kg in Andosols (Takeda et al., 2004).

Low V contents are mainly in soils of light texture (Table 10.2). V in soils seems to be associated especially with Fe hydrous oxides and SOM. In some soils, clay minerals can also control the mobility of V. Apparently, the most common form of V in soils is the vanadyl cation (VO^{2+}), which predominates in acid soils and is likely to be mobilized as complexes with organic acids. Anionic forms of this metal, VO_3^- , VO_4^{2-} , and H_2VO_4^- , occur rather in neutral and alkaline soil solutions (Kabata-Pendias and Sadurski, 2004). Anionic species of V can be relatively easily absorbed by clay minerals, especially together with Fe cations. This might explain considerable concentrations of V in various concretions and nodules formed in soils: 400 mg/kg in Fe-rich and 440 mg/kg in Mn-rich nodules. However, Berrow et al.⁷¹ emphasized that in certain horizons of Podzols, the role of clay minerals as well as organic acids might be more significant in V speciation than V fractions adsorbed by Fe oxides.

During weathering, the mobility of V is dependent on the host minerals, and finally V remains in the residual rock-forming minerals or is adsorbed or incorporated in mineral structures of clays or Fe oxides. A high degree of association of V with Mn and with the K content of soil has also been reported by Norrish.⁵⁷⁰

Although there are not many reports of V pollution of soils, it is likely that industrial processing of certain mineral ores (ore smelters, cement, and phosphate rock plants) and burning of coals and oil will increase the deposition of V in soils. Combustion of fuel oils is an especially serious source of V in soil. Soils in areas of metal smelters have increased V levels up to 80 mg/kg, and in the vicinity of an oil refinery, above 80 mg/kg.¹³⁹⁰ Surface soils polluted by fly ash contain V up to 429 mg/kg (Morrell et al.¹⁰⁹⁵). Tyler⁸¹⁴ reported that forest more around a densely inhabited area accumulated V up to 100 mg/kg, and Pawlak⁶⁰⁵ found increased V content of soil up to 110 mg/kg in the vicinity of a crude oil refinery. Belsare⁹³⁶ determined V contents in soils surrounding a thermal power station at a graphite industry in India, within the range of 350–840 mg/kg. Jacks³⁴⁷ calculated that the V aerial input to soil in the vicinity of Stockholm is approximately 20 mg/m²/year.

C PLANTS

Vanadium is relatively easily taken up by plants through root systems from acid soils, and presumably it is absorbed passively as indicated by the linear function of its content in plants *versus* its concentration in soil solution (Figure 10.1). These results indicate that VO^{2+} species occurring under acid conditions are more rapidly absorbed by roots than are V_3^- and HV_4^{2-} species that predominate in neutral and alkaline solutions. Apparently, cationic species of V are easily available to plants than anionic species; however, both species are capable of being chelated and thus could contribute substantially to the V uptake by plants from soils.⁸⁵⁹ The biotransformation of vanadates (VO_3^-) to vanadyl (VO^{2+}) during uptake by plants has been observed.¹⁰⁹⁵

The essentiality of V for alga species and certain bacteria has been demonstrated, although it is not yet considered to be an essential element for higher plants. There are evidences that V is a specific catalyst of the N_2 fixation and may partially substitute for Mo in this function, in particular, when carried on by rhizobium bacteria. Dobritskaya¹⁸⁰ reported a high accumulation of V in nodules of several legumes (3–12 mg/kg), which suggests the V association with the N_2 biofixation. However, no evidence of the V deficiency in higher plants was observed, and Welch and Cary⁸⁶⁰ claimed that if V is essential for plants, adequate levels in their tissues are less than 2 ($\mu\text{g/kg}$).

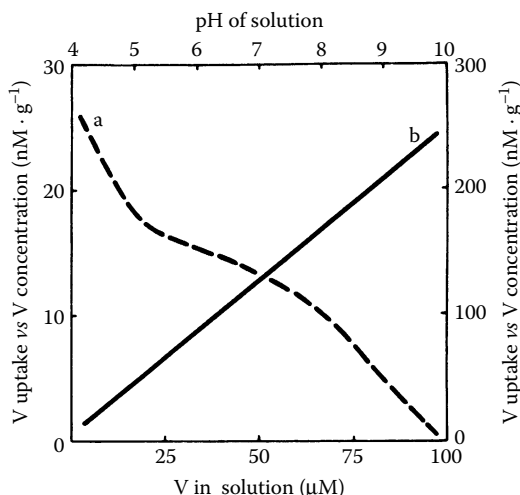


FIGURE 10.1 The influence of (a) pH on the rate of V absorption by barley roots from a solution of mM NH_4VO_3 ; (b) V concentration in the solution on its content in barley roots. (From Welch, R. M., *Plant Physiol.*, 51, 828, 1973. With permission.)

Piispanen and Ländesmäki¹¹²⁰ found that the amount of blue-green algae increases in relation to the amount of green algae with increasing V concentration, and algal mixture (blue-green) tolerates a higher content of V_2O_5 in the solution than green algae alone. The enzymes found in some algae (V-Br-peroxidase) are involved in the process of the reduction of hydrogen peroxide due to the alteration from V^{3+} to V^{5+} . In general, the coefficient of V enrichment in algae was relatively high, and therefore these authors concluded that some water plants may be useful as indicators for V occurrence.

Contents of V in food plants vary broadly, from about 10 to 700 $\mu\text{g}/\text{kg}$, and do not show any clear regularity in the distribution among plant species and plants organs. The highest reported contents of V are related to the V-polluted areas in Germany (Anke et al., 2003). Several mushroom species contain elevated amounts of V, up to about 1000 $\mu\text{g}/\text{kg}$ (Table 10.3). Petrunina⁶¹³ reviewed this topic and showed that some bryophytes and fungi, especially *Amanita muscaria*, may contain as much as about 180 mg/kg, when grown in mineralized areas. Other accumulator plant species are also known.¹¹⁹ The sporophore of *Amanita muscaria* in unpolluted woodland is reported to contain V up to 345 mg/kg, although the total V in the soil was relatively low (6.7 mg/kg).¹⁰⁶⁰

Mosses collected in Norway during 1990–1995 contained V in the range of <0.01–16 mg/kg, at an average value of 2.8 mg/kg.¹²²³ The V content of moss samples from the vicinity of peat-fired plant was up to 8 mg/kg, and vegetables grown close to the thermal power station contained up to 4.9 mg/kg. Moreover, grasses and clovers, grown in surroundings of the crude oil refinery contain V within the range of 8–13 mg/kg, respectively.¹³⁵⁷

There is not much evidence for the V toxicity to plants. Increased concentration of V (up to 3 mg/kg) in the nutrient solution under greenhouse conditions is reported to reduce the length of collard roots by 50% (Gettier et al.¹⁰¹⁰). Symptoms of V toxicity (chlorosis and dwarfing) may appear at about its content of 2 mg/kg in some plants. The reduction of elevated V content in plants is of a great significance since V^{5+} is recognized as a potent inhibitor of several enzymes, which are largely unaffected by the reduced V^{4+} . There is also some evidence that V is a specific catalyst of the N fixation and may substitute for Mo, particularly in rhizobium bacteria. Evidence for this comes from the observed, Dobritskaya,¹⁸⁰ accumulation of V (up to 12 mg/kg) in nodules of several legumes.

The values given by Shacklette et al.⁷¹⁰ for V in some food plants are as follows (in $\mu\text{g}/\text{kg}$ FW): lettuce, 1080; apple, 330; potato, 1490; carrot, 990; beet, 880; and pea, 460. These values are much higher than those presented in Table 10.3 and apparently reflect a pollution source of V.

TABLE 10.3
Vanadium in Food Plants^a (μg/kg)

Plant	Range	Mean
Wheat, grain	7–10	9
Winter wheat grain ^b	0.6–7.8	2.2
Barley ^b	0.9–7.6	3.4
Oats, grain	—	60
Asparagus	52–128	—
Lettuce, leaves	280–710	300
Onion, bulbs	22–58	—
Cucumber	35–56	40
Potato, peeled	458–606	—
Parsley, roots	—	360
Spinach ^c	533–840	—
Wild mushrooms ^c	50–2000	—
Apple, fruits	—	320
Lemon, fruits	—	110
Caraway, seeds	—	430
Black pepper, seeds	—	985

^a Adapted from Kabata-Pendias and Pendias,¹³⁵⁷ Anke et al. (2003).

^b Data for Sweden, after Eriksson (2001).

^c Data for the United States (ATSDR, 2002).

Bryophytes appear to be most sensitive to aerial sources of V. Bowen⁹⁴ gave the mean V content of mosses as 11 mg/kg. Shacklette and Connor (see Cannon et al.¹¹⁹) found the range of V in Spanish moss to be 50–180 mg/kg AW, being higher in areas affected by emissions from crude oil refining. Gough and Severson²⁷⁸ found V to be as high as 700 mg/kg AW in sagebrush near a P fertilizer plant. Pawlak⁶⁰⁵ reported the mean V content of clover and grass grown in the vicinity of a crude oil refinery to be 13 and 8 mg/kg, respectively. Folkesson²³⁹ found the range in V concentration in mosses near a peat-fired plant to be 6–8 mg/kg and in those near the ash heap to be 14–25 mg/kg. Belsare⁹³⁶ reported that vegetables grown in the vicinity of a thermal power station contained V within the ranges 1.9–4.9 mg/kg (cabbage) and from 0.8 to 1.7 mg/kg (tomato).

Gough et al.²⁷⁹ reviewed the topic of V phytotoxicity and stated that there are no reports indicating its toxicity under field conditions. However, under man-induced conditions, V concentrations as high as 0.5 mg/kg in the nutrient solution, and 140 mg/kg in the soil solution, may be toxic to plants. Gettier et al.¹⁰¹⁰ reported that in greenhouse conditions, V (as vanadyl sulfate) at a concentration of 3 mg/kg in the solution reduced the length of collard roots by 50%. The V toxicity to plants varies with soil types due to the variable phytoavailability. In sandy soil, 80 mg/kg V can reduce plant growth; whereas in loamy soil, >100 mg/kg V does not affect plants. Phytotoxicity of V may appear at a concentration of about 2 mg/kg in some plants, as cited by Davis et al.¹⁷¹ Wallace et al.⁸⁴¹ reported that bush beans absorbed V from culture solution as much as 13, 8, and 880 mg/kg in leaf, stem, and root, respectively, and that this resulted in a smaller growth but not in chlorosis.

II NIOBIUM

A INTRODUCTION

Niobium, also called columbium (Cb), is relatively common in the terrestrial environment, at an average content of 20 mg/kg in the Earth's crust and average of 12 mg/kg in worldwide soils

(Table 3.2). The amounts of Nb increase in acid igneous rocks and in argillaceous sediments (Table 10.2).

The +5 valence state of Nb is the most stable and its compounds are slightly mobile in terrestrial environments. In the nature, Nb and Ta occur together because of their similarities in some properties and atomic radii (Table 10.1), and both exhibit the affinity to associate with Fe, Ti, and Zr. Nb is scattered in several minerals of complex formula, like, for example, columbite/niobite, $(\text{Fe,Mn}) \cdot (\text{Nb,Ta})_2\text{O}_6$, and pyrochlore, $(\text{Na,Ca})_2(\text{Nb,Ta})_2\text{O}_6(\text{OH,F})$. Coltan is a metallic ore containing columbite–tantalite mixture from which Nb and Ta are extracted. Nb is also included in the crystal lattices of Ti-minerals and in minerals bearing the LAs. Moreover, Zr is known as a carrier of Nb in igneous rocks (Fairbridge, 1972). The average Nb content in the U.S. coal is estimated as 2.9 mg/kg, with the maximum level of 70 mg/kg (Finkleman, 1999).

Annual global production of Nb in 2008 was calculated as 60 kt (USDI, 2009). This metal is used mainly for steel alloys. Nb-containing alloys are resistant to strength and to cryologic factors, and therefore are widely used in pipeline constructions and in aerial transportation industries. These alloys are also superconductive. Because of special properties, Nb is added to alloys used for surgical implants as well as in the stomatology. It is also used as a precious metal, often with Ag and Au.

B SOILS

The behavior of Nb during weathering is highly dependent on host minerals; therefore, Nb may be released (e.g., from biotite and amphibolite) or may remain within resistant minerals (e.g., sphene and zircon). The accumulation of Nb in certain residual sediments has often been reported. Most of the Nb compounds are slightly soluble in both acid and alkaline media. However, the presence of organic complexing agents mobilizes Nb.

There are not many reports on the Nb status of soils. The geometric means of 12.5 mg/kg Nb has been calculated for surface soil samples of the United States. The highest contents of Nb are in Cambisols, especially derived from rocks enriched in this metal (Ure et al.⁸¹⁹). Gough et al.¹⁰¹² found Nb in various soils of Alaska to range from <4 to 44 mg/kg, with a geometric mean of 8 mg/kg. Ure and Bacon⁸¹⁸ reported a mean Nb content of 24 mg/kg for standard soil samples, whereas Ure et al.⁸¹⁹ gave the range in Nb concentrations in arable soils of the United Kingdom derived from different rocks, as 31–300 mg/kg. Wedepohl⁸⁵⁵ stated that Nb averaged 24 mg/kg in lateritic soils from West Africa. Govindaraju¹³¹³ reported the Nb content in reference soils of China to range from 9.3 to 37.6 mg/kg, and in reference soils of the United States, within the range 6.4–22.0 mg/kg. Kadunas et al.¹³⁵⁹ gave the median value of 12.5 mg/kg for Nb in the Lithuanian soils. Agricultural soils from Sweden contain Nb within the range of value from 5 to 17 mg/kg, at an average of 12 mg/kg (Eriksson, 2001). The median Nb contents in rural soils of Japan vary from 6.3 mg/kg in Andosols to 14 mg/kg in Cambisols (Takeda et al., 2004).

C PLANTS

Niobium is reported to be relatively mobile under humid conditions and therefore may be available to plants. The common range of Nb in food plants is 0.02–1.1 mg/kg. Cereal grains of Sweden contain Nb in the range from 0.5 to 1.7 mg/kg (Eriksson, 2001). Its contents in herbs liquorice (*Glycyrrhiza uralensis*) from the Ural Mountains range (in mg/kg) from 0.14 to 1.0 (average 0.4) and from 0.4 to 2.1 mg/kg (average 1) in roots and in tops, respectively (Grankina et al., 2003). Tiutina et al.⁸⁰⁰ found that the common value of Nb in plants is about 1 mg/kg; however, several native plants have a great capacity for extracting Nb from soil that is enriched in this metal. Concentrations of Nb up to about 10 mg/kg are reported for selected plant species (mainly *Rubus arcticus* L.) from an Nb mineralized area of Komi (former Soviet Union) and is proposed as an exploration indicator for Nb-ore deposits.¹³⁵⁷

Niobium in moss sampled in Norway in 1990–1995 ranged between <0.002 and 0.8 mg/kg and averaged 0.11 mg/kg.¹²²³ Its contents have not changed much during the recent decades.

III TANTALUM

A INTRODUCTION

The mean Ta content of the Earth's crust is established at 2 mg/kg (Table 3.2). The highest abundance of Ta, up to 4 mg/kg, is in acid igneous rocks and the lowest in calcareous sedimentary rocks, up to 0.05 mg/kg (Table 10.2). Ta exhibits both lithophilic and chalcophilic properties and occurs in few minerals, mainly oxides, in the association with Nb, Ti, Y, LAs, as well as with other metals. Tantalite, (Fe,Mn)(Ta, Nb)₂O₆, is the most important mineral for Ta extraction. Other, also common, Ta minerals are formanite YtaO₄, and mikrolithe (Ca,Na)₂(Ta₂O₆)(O,OH,F). This metal is nearly always found in association with Nb. The host minerals for Ta in igneous rock types include pyroxene, amphibole, biotite, ilmenite, and sphene. Minerals such as sphene and ilmenite contain the highest concentrations of Ta (250–350 mg/kg), whereas pyroxene minerals contain much less (<7 mg/kg).

Geochemical properties of Ta are fairly similar to those of Nb, but it is less mobile than Nb because of a lower solubility during weathering processes and a slight stability of organic complexes. It is likely to be concentrated in argillaceous sediments and in Fe-enriched sea-bottom sediments.

Global Ta production in 2008 was calculated as 815 tons (USDI, 2009). The major use of Ta is in the production of several electronic components applied in various industries. Due to its high melting point and good ductility, Ta is a component of super alloys used for jet engines, nuclear reactors, and missile parts. Metallic dust of Ta is a fire and explosion hazard. This metal is totally immune to the action of body liquids and therefore is widely used in surgical appliances (e.g., Ta coatings are used in the construction of orthopedic implants due to its ability to form a direct bond with hard tissue).

B SOILS

The Ta distribution in rocks follows that of Nb and reaches the highest concentrations in acid magmatic rocks (2–4 mg/kg) and in argillaceous sediments (1–2 mg/kg) (Table 10.2).

According to data presented by FOREGS (2005), Ta in worldwide soils averages 1.1 mg/kg. Reported Ta levels in various soils are within the range of 0.17–3.9 mg/kg. Ta contents in reference soils of China range from 0.8 to 5.3 mg/kg, and in reference soils of the United States, from 0.7 to 1.2 mg/kg (Govindaraju¹³¹³). The 90th percentile for Ta in Finnish soils is about 1.5 mg/kg.¹³⁶⁸ The Ta contents of deep loess deposit in the European part of Russia average from 1 to 2 mg/kg (Vaganov and Nizharadze¹⁸¹). Agricultural soil from Sweden contains Ta in the range of 0.5–1.6 mg/kg, at an average of 1.1 mg/kg (Eriksson, 2001). Median levels of Ta in rural soils of Japan range from 0.7 to 1.4 mg/kg, being the highest in Gleysols (Takeda et al., 2004).

C PLANTS

Oakes et al.⁵⁷⁴ found the range of Ta in food plants to be from 0.013 to 0.48 µg/kg FW, whereas Bowen⁹⁴ gave the mean Ta in edible parts of vegetables as <1 µg/kg. Laul et al.⁴⁶² reported Ta in vegetation from <1 to <6 µg/kg. Cereal grains (wheat and barley) from Sweden contain Ta in the range of 1.1–5 µg/kg, with smaller amounts in wheat than in barley (Eriksson, 2001).

11 Elements of Group 6 (Previously Group VIb)

The trace metals of Group 6, chromium (Cr), molybdenum (Mo), and tungsten (W), have strong lithophilic tendencies. They have variable oxidation states, possess bimodal redox behavior in terrestrial and aquatic environments, and are likely to be present in two oxidation states, +3 and +6 (Table 11.1). Metals of this group have the propensity to form oxyanions and coordinate only weakly with other common environmental ligands such as Cl^- or OH^- .

The geochemical behaviors of Mo and W are very similar.

I CHROMIUM

A INTRODUCTION

The abundance of Cr in the Earth's upper crust averages 100 mg/kg (Table 3.2). The distribution pattern of Cr in rocks shows the tendency to its concentration in mafic igneous rocks and in argillaceous sediments (Table 11.2). In ultramafic rocks its content can be over 3000 mg/kg and in acid ones (e.g., granites) may be less than 50 mg/kg.

Chromium is precipitated from magma at an early stage, in the chromiun spinel mineral groups, with the general formula, $(\text{Mg,Fe})\text{O} \cdot (\text{Cr,Al,Fe})_2\text{O}_4$. All Cr minerals are resistant to chemical weathering and due to their high specific gravity are usually concentrated in various types of intrusions and deposits. Cr-minerals are likely to be associated with pyroxenes, amphibolites, and micas. Chromite, FeCr_2O_4 and crocoite, PbCrO_4 are relatively common minerals. The geochemical association of Cr with Fe and Mn is responsible for its elevated concentrations in ferromanganese nodules of sea bottom sediments as well as in Fe-concretions of soils.

The speciation of Cr is Eh–pH dependent under most environmental conditions. The variable properties of Cr have been described in several fundamental publications (e.g., Bartlett,¹²¹⁸ James et al.,¹³⁴³ Barnhart, 1997; Kotaś and Stasicka, 2000). The geochemistry of Cr is complex because of its easy conversion from one oxidation state to another. Daulton et al. (2007) described significant role of metal-reducing bacteria (*Shewanella oneidensis*) in Cr^{6+} Cr^{2+} reducing process.

Global production of Cr in 2008 is reported at 21.5 Mt (USDI, 2009). The main use of Cr is in metallurgical, refractory and chemical industries, however, it was first used as a pigment because of its yellow color.

The major proportion of Cr is used for stainless steel and chromate plating. In the chemical industry, Cr (both +3 and +6) is used primarily in pigments, metal finishing, and wood preservatives. It is commonly used in the manufacture of green tints for paints, varnishes, glazes, and inks. Leather tanning utilizes especially substantial amounts of Cr compounds. This metal is used in various phases of paper manufacture.

The main source of Cr pollution is considered to be from dyestuffs and leather tanning when wastes are discharged directly into waste streams, either as liquids or solids. Sewage treatment plants from industrial and residential sources discharge substantial amounts of Cr. Thus, chromite-ore processing residue (COPR) is of the greatest environmental risk in some regions.

TABLE 11.1
Selected Properties of Trace Elements of Group 6

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C, g/cm ³)	Valence ^b
Cr, chromium	24	51.9	185	7.19	+2, +3 , +4, +5, +6
Mo, molybdenum	42	95.9	201	10.2	+2, +3, +4, +5, +6
W, tungsten	74	183.8	202	19.3	+2, +3, +4, +5, +6

^a Approximately average values for main oxidation states.

^b Valence values in bold are for the main oxidation states.

B SOILS

The world soil average content of Cr in soils has been established as 60 mg/kg (Table 3.2). Since soil Cr is inherited from parent rocks, higher contents are generally found in soils derived from mafic rocks and argillaceous sediments. Soils developed from serpentines are especially elevated in Cr, sometimes to above 100,000 mg/kg. Salvador-Blanes et al. (2006) emphasized the impact of geological origin of weathered bedrocks on the distribution of Cr in soil profiles. According to this observation, Cr contents of weathered bedrocks (16–355 mg/kg) are higher than in topsoils (31–129 mg/kg). However, data presented by Čurlík and Šefčík (1999) indicate that high Cr levels (up to 6096 mg/kg) are in both, A and C horizons of soils from Outer Carpathians.

The behavior of soil Cr has been extensively studied by Bartlett and Kimble,⁵¹ Bartlett and James,⁵⁰ Cary et al.,¹²² Bloomfield and Pruden,⁸² and Grove and Ellis,²⁸⁹ and by James et al.¹³⁴³ and

TABLE 11.2
Abundance of Cr, Mo, and W in Rocks and Soils (mg/kg)

Rock/soil	Cr	Mo	W
Earth's crust	126–185	1.1	1
Igneous rocks	—	—	—
Mafic	170–3400	0.2–1.5	0.3–1.1
Acid	10–50	1–2	1.3–2.4
Sedimentary rocks	—	—	—
Argillaceous	80–120	2–2.5	1.8–2
Sandstones	20–40	0.2–0.8	0.3–2
Calcareous	5–16	0.2–0.4	0.3–0.6
Soils ^a	60 ^b	1.1 ^b	1.7 ^b
Arenosols (sandy)	2–360	0.1–3.7	0.7–2.7 ^c
Podzols (medium loamy)	10–300	0.4–6.4	0.6–3.4 ^d
Cambisols (heavy loamy)	30–1100	0.7–7.2	—
Calcisols (calcareous)	22–500	0.3–7.4	—
Histosols (organic)	15–170	0.3–3.2	—

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil average (Table 3.2).

^c Data for various soil groups.

^d Data for soils of Parana, Brazil [Licht O.A.B. (ed) 2005. *Geochimica de solo do Estano do Parana*. Vol 1/2. Mineropar, Curidiba, Parana (in Spanish)].

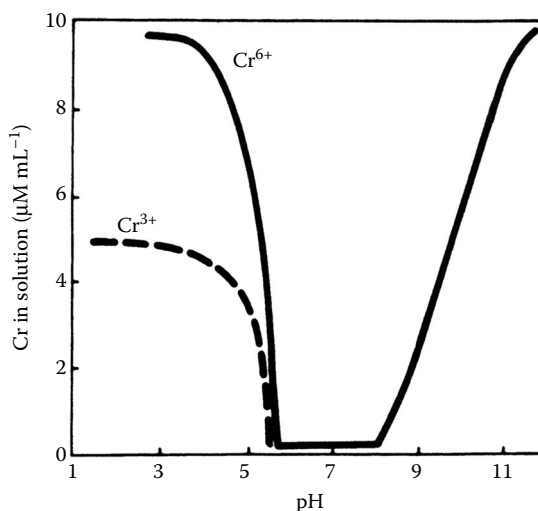


FIGURE 11.1 Solubility of trivalent and hexavalent Cr as a function of pH. (From Bartlett, R. J. and Kimble, J. M., *J. Environ. Qual.*, 5, 379 and 383, 1976. With permission.)

Bartlett.¹²¹⁸ Since Cr^{3+} is slightly mobile only in very acidic media, and at pH 5.5 it is almost completely precipitated, its compounds are considered to be very stable in soils. On the other hand, Cr^{6+} is very unstable in soils and is easily mobilized in both acid and alkaline soils (Figure 11.1). However, Cr occurs in soils mainly (>80% of total content) in the immobile residual fraction. A positive relationship between Cr and the fine granulometric fraction in soils has resulted in a higher Cr content in silty and loamy soils than in sandy ones (Table 11.2). Some of the highest Cr contents are reported for loamy and clay soils of Chad (100–300 mg/kg),³⁹ for loamy soils of New Zealand (70–1100 mg/kg),⁸⁶¹ and for forest soils of Bulgaria (152–384 mg/kg).⁵⁵⁸ Swedish arable soils contain Cr in the range from 3 to 50 mg/kg, at an average value of 22 mg/kg (Eriksson, 2001). The median Cr contents in agricultural soils of Japan vary from 56 to 70 mg/kg, in Andosols and Acrisols, respectively (Takeda et al., 2004). In Finnish soils, the 90th percentile for Cr soluble (leached) in acids (HNO_3 , HCl) is given as 50 mg/kg, while the 90th percentile of Cr-total content (fusion H_2F_2) is 150 mg/kg.¹³⁶⁸ Peat exhibits a high sorption capacity for Cr, in the range of values from 24,250 to 52,800 mg/kg, and bind this metal mainly as an insoluble metal-organic complex (Kyzioł, 2002).

The highly variable oxidation states of Cr allow the formation of complex anionic and cationic species, as well as organic complexes. Naturally occurring Cr compounds have principal valences of +3 (chromic) and +6 (chromate). Highly oxidized Cr forms are much more mobile than Cr^{3+} species, especially under very acidic and alkaline ranges of pH (Figure 11.1).

The complex ion species mobile in soil environments are: CrOH^{2+} , CrO_4^{2-} , HCrO_4^- , HCrO_3^{2-} , $\text{Cr}(\text{OH})_4^-$, and $\text{Cr}(\text{CO}_3)_3^{3-}$ (Kabata-Pendias and Sadurski, 2004). In the contrary, the species $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, is considered relatively inert due to the slow exchange of hydration water (Raspor, 2004). Cr reveals a great capability to form various organic complexes. Thus, ionic Cr species are highly susceptible to oxidation–reduction processes that govern the behavior of this metal in soils (Bartlett¹²¹⁹). Soil pH has an influence on the Cr speciation and solubility. In uncontaminated (pristine) soils at neutral pH, Cr is slightly mobile and thus not easily available to plants which may have nutritional implications. However, several soil factors, and especially organic substances have a crucial impact on Cr forms and behavior. Under natural soil conditions, Cr oxidation potential seems to be directly related with Mn-oxide contents (Chung and Sa, 2001).

El-Bassam et al.²⁰⁵ observed that under the same redox potential (500 mV), Cr^{3+} predominated at pH 5, $\text{Cr}(\text{OH})_3$ was formed between pH 5 and 7, and CrO_4^{2-} occurred at pH > 7. The rapid conversion of the Cr oxidation state is closely associated with Fe and Mn oxidation–reduction processes in soils

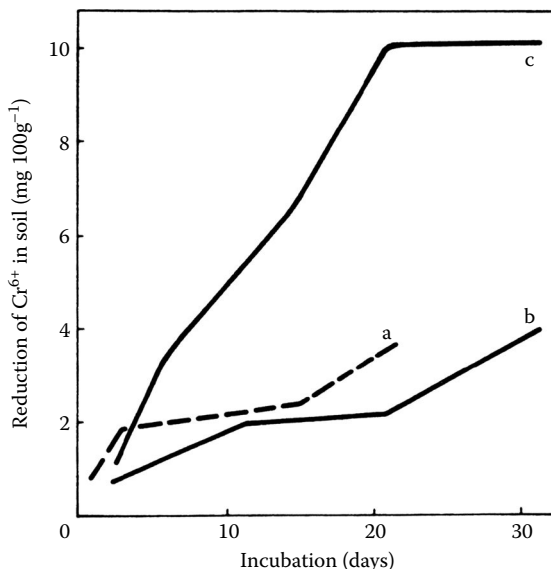


FIGURE 11.2 Reduction of Cr⁶⁺ by soil (pH 6.7) during the incubation. (a) aerobic; (b) anaerobic; (c) anaerobic with added dry alfalfa material. (Reprinted from Bloomfield, C. and Pruden, G., *Environ. Pollut.*, 23a, 103, 1980. With permission.)

(James et al.,¹³⁴³ Geelhoed et al., 2003). The reduction of Cr⁶⁺ can lead to two general types of products: soluble Cr³⁺-organic compounds or Cr-hydroxide precipitates, Cr_{1-x}Fe_x(OH)₃ (Fendorf et al., 2002, 2004). However, biological reduction or reduction by organic molecules has the potential to form soluble Cr³⁺-organic complexes.

The behavior of Cr in soils may be modified by organic complexes of Cr; however, the dominant effect of OM is the stimulation of the reduction of Cr⁶⁺ to Cr³⁺ (Figure 11.2). Biogenic Fe²⁺ is also involved in the reduction of Cr⁶⁺. Due to the ease in variability of the oxidation state of Cr, this metal is used for the standard spot plate field test for the oxidation potential in soils (Bartlett¹²¹⁹). Wittbrodt and Palmer¹⁵⁴⁵ investigated the reduction of Cr⁶⁺ by soil HA, and described the difference between the rate coefficients for the HA and FA even from the same soil. Organic substances added as sewage sludge to the soil (loamy sand, pH 6.1) caused a significant increase of two Cr species—associated with hydrous oxides and bound to OM (Figure 11.3). The Cr³⁺ bound to both

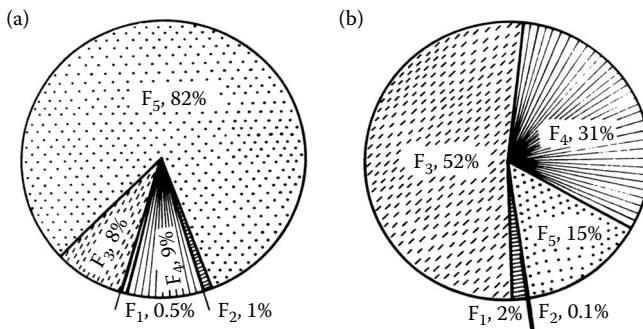


FIGURE 11.3 Variation in Cr species in soils under sludge application. (a) unsludged soil, (b) sludged soil. Cr species: (F₁) easily soluble; (F₂) exchangeable; (F₃) associated with hydrous oxides; (F₄) bound to organic matter; and (F₅) residual. (From Dudka, S. and Chlopecka, A., *Water Air Soil Pollut.*, 51, 153, 1990. With permission.)

HA and FA is easily mobilized; bound to HA is mobile at higher pH values than that fixed by FA (Laborga et al., 2007).

The sorption of Cr in soil is associated primarily with clay contents, and to a lesser extent with Fe hydroxides and SOM. However, the impact of SOM on the conversion, and particularly on the reduction of Cr (especially Cr^{6+} to Cr^{3+}) is of a great environmental significance, and has been studied widely Bartlett,¹²¹⁹ Barnhart (1997), James et al.,¹³⁴³ and James (2001) described the $\text{Cr}^{3+}/\text{Cr}^{6+}$ balance of exchange as an oscillating “seesaw” with available Mn and OM, where the soil pH acts as a controllable master variable that helps to set the oxidizing reactivity of Mn oxide *versus* the reducing properties of OM and other compounds (e.g., Fe, S). This author also has described the variability of Cr ions as affected by the oxidation–reduction potential of soils amended with various wastes, particularly those containing OM.

Forms and transformation of Cr in soils have great environmental and health implications. Therefore, the speciation of Cr in soils and its solubility in Cr-polluted soils have been widely studied (Barnhart, 1997; Rüdél et al., 2001). The conversion of Cr species in soils can be relatively rapid and significant. Dudka et al. (1993) demonstrated that OM added as sewage sludge to the soil (loamy sand, pH 6.1) caused significant variation in Cr species: exchangeable forms increased from 8% to 52%, and OM-bound forms increased from 9% to 31% of the total Cr content. Such concentrations of mobile Cr can be toxic to crop plants. In highly Cr-polluted soils in Mexico, total Cr contents in the surface layer varies between 807 and 12,960 mg/kg and is concentrated mainly in two fractions; reducible hydrous Fe–Mn oxides and oxidizable sulfides and organic phases (Armienta et al., 1996).

In ultramafic soils, where a large part of Cr occurs mainly in insoluble phases, Cr was present in the soil solution, under natural vegetation, in the range of 2.7–10 $\mu\text{g/L}$, whereas under crop vegetation, due to effects of phosphorous fertilizers, its concentrations reached up to 700 $\mu\text{g/L}$ (Becquer et al., 2003).

Activities of soil microbial enzymes decreases under increased Cr-levels in soils; dehydrogenase activity and nitrification processes are especially sensitive (Pacha, 1989; Rüdél et al., 2001). Hexavalent Cr compounds exhibit a strong mutagenic effect on *Bacillus subtilis*, while Cr^{3+} compounds are only slightly mutagenic to that microbial species.¹¹¹⁰ The response of soil bacteria to Cr^{3+} is species dependent, that is, while *Rhizobium* sp. and *Bradyrhizobium* sp. do not tolerate any Cr^{3+} , the growth of other soil bacteria is stimulated by its concentrations (0.2–5 mg/L) (Wyszkowska and Kucharski, 2004). The toxic effects of chromate in bacteria are because of the oxidative damage to biomolecules. Several microorganisms are resistant to Cr^{6+} due to chromate reduction processes (Ramirez-Diaz et al., 2008).

Soil Contamination and Remediation. The Cr content of surface soils is known to have increased due to pollution from various sources, of which the main ones are COPR, pigments and tannery wastes, leather-manufacturing wastes, and municipal wastes. A number of studies have been recently carried out to understand the environmental problems and effectiveness of remedial treatments of Cr-contaminated land (Bini et al., 2008; Geelhoed et al., 2003; Hiller et al., 2003). Land contaminate with COPR (millions of tons of COPR in the past have been deposited in lands around Cr industries) has recently become of great environmental concern (Farmer et al., 1999).

Municipal and industrial wastes from various sources may contain elevated amounts of Cr, up to 10,200 mg/kg, at an average of 1993 mg/kg (Maján et al., 2001). Its contents in sewage sludge (mainly municipal wastes) applied to agricultural soils usually vary between 100 and 200 mg/kg. The deposition rates of Cr to agricultural soils have been calculated as 0.5–46 g/ha/year, being the lowest in Finland and the highest in Italy (Nicholson et al., 2003). As estimated by these authors, the total annual input of Cr to agricultural land in England and Wales in 2000 was 327 tons of which 126 tons was from inorganic fertilizers (mainly phosphate), 83 tons from atmospheric deposition, and 78 tons from sewage sludge. Bini et al. (2008) reported that mean Cr concentration in soils of the leather tannery in Italy is 210 mg/kg (range 50–10,000). Biosorption of Cr by bacteria (*Pseudomonas* spp.) from tannery effluents is effective in reducing elevated contents of this metal (Srivastava et al., 2008). Topsoils around electroplating industries in Portugal contain Cr up to

27,132 mg/kg, at an average of 1000 mg/kg (Morgado et al., 2001). Soils surrounding the Cr smelter in Albania contain this metal, at average, 3117 mg/kg, whereas its highest concentration, up to 20,300 mg/kg, is in soils close to the slags (Shtiza et al., 2005).

On the worldwide basis, the disposal of commercial products that contain Cr may be the largest contributor, accounting for about 51% of the total Cr released to soil. The disposal of coal fly-ash and bottom fly-ash contribute more than 30% of Cr to soil (Nriagu and Pacyna, 1988).

Farmlands amended with sewage sludges are likely to be enriched in Cr, especially because Cr is usually accumulated at the thin top layer of soils. Cr, as all other micro-cations, is not distributed uniformly in soils, but is likely to be concentrated in nodules and concretions. Nodules separated from the COPR-contaminated soils near Glasgow, Scotland, contain elevated amounts of Cr between 14,700 and 36,400 mg/kg, whereas, the whole surface soil layer (20–40 cm) averaged 16,200 mg Cr/kg (Farmer et al., 1999).

El-Bassam et al.²⁰⁵ found that after 80 years of irrigation with sewage sludge containing 112 mg/kg Cr, the metal concentration in soil increased from 43 to 113 mg/kg. Other authors also reported a high Cr accumulation for surface horizons of sludged farmland, where the highest Cr levels ranged from 214 to 727 mg/kg.^{59,176,314,1173} Especially contaminated surface soils were found in a proximity of Cr smelter heaps where the metal concentration exceeds 10,000 mg/kg.¹¹⁷³ Surface soil from the reclaimed land (1-m-deep layer above the Cr slag deposit) in Japan contains up to 4560 mg/kg Cr⁶⁺ (DW) due to the movement of this cation with capillary water and despite earlier reduction of Cr⁶⁺ to Cr³⁺ with FeSO₄ in the surface layer of the slag.⁹²⁶ Izasáki et al.¹⁰³⁵ reported the movement of Cr pollutants to deeper layers of the sandy soil, where it was detected in groundwater at a depth of 2–3 m.

Chaney et al.¹³⁰ extensively discussed the Cr hazard in biological waste management and stated that the food chain is well-protected from an excess of Cr by the “soil-plant barrier.” This statement, however, is not fully supported by the findings of Diez and Rosopulo,¹⁷⁶ who reported the ready availability of Cr from soils amended with sewage sludge. Solubility and toxicity characteristics of Cr³⁺ and Cr⁶⁺ in soil present a challenge for the establishment of MAC value by regulatory agencies. The rule proposed (“Hazardous Waste Identification Rule”) establishes the cumulative land application limit at 3000 kg Cr/ha, based on data showing no effects on plants (NOEC) at this maximum level of Cr used in a field study.¹³⁴³ However, the Cr valence state and soil conditions for oxidizing Cr³⁺ should be considered.

The main purpose of remediation treatments of Cr-contaminated soils is the conversion of easily mobile Cr⁶⁺ to Cr³⁺. Both Cr species occur in COPR, which has a pH between 11 and 12, and is associated with various mineralogical phases. Most minerals, for example, carbonates, oxides, and silicates exhibit a strong capacity to accommodate significant amounts of Cr. Due to specific geochemical properties of COPR, ferrous sulfate has appeared to be not effective enough in the reduction of Cr⁶⁺ (Hiller et al., 2003). Geelhoed et al. (2001, 2003) have emphasized that each Cr-contaminated site has to be studied to evaluate the adequacy treatments designed using the model ORCHESTRA-CHROMIUM, based on the chemical equilibrium and precipitation/dissolution reactions of various mineral phases.

Some recent studies have been focused on the effect of organic compounds (carbon) on the reduction of Cr⁶⁺ to Cr³⁺. Tzou et al. (2003) reported that in surface soils this reduction is highly accelerated even when artificial light is available, whereas Tokunaga et al. (2003) indicated an increased reduction of Cr⁶⁺ due to microbial activities after the addition of organic carbon to heavily contaminated soils. Alcântara and Camargo (2004) reported an increased Cr movement in the A soil horizon, possibly due to the formation of soluble compounds with FA. Great affinities of zeolite (synthesized) and zero-valent-Fe NP for sorption of various Cr species have also been reported (Xu and Zhao, 2007; Sui et al., 2008). Montmorillonites (pillared clays) reveal great adsorptive properties for Cr³⁺ that increase with pH (Bakhti et al., 2001).

Varieties of treatments have been applied with different effects depending upon specific geochemical conditions of Cr-contaminated sites. Some of the remediation treatments are as

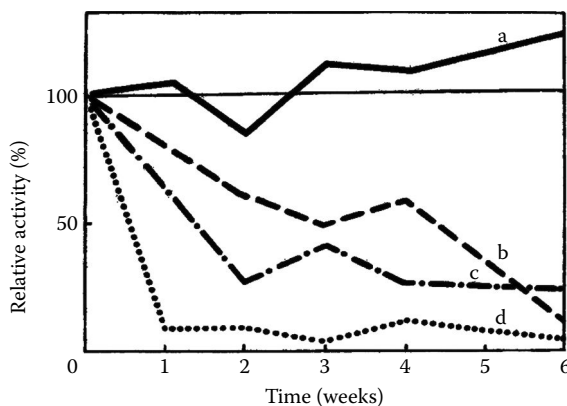


FIGURE 11.4 Enzymatic activity of beech forest soil as affected by Cr^{3+} (2000 mg/kg Cr as CrCl_3). Activity: (a) amylolytic; (b) alkaline phosphatase; (c) acid phosphatase; and (d) dehydrogenase. (Modified from Pacha, et al. *Acta Biol. Sil., Katowice*, 9, 38, 1988.)

follows: (1) immobilization of Cr using materials of high sorption capacity, for example, smectite clays, coal, bone charcoal (or other sorbents), (2) removal of Cr by electrokinetic techniques, (3) reduction of Cr^{6+} by ferrous sulfate and/or sulfate-reducing bacterial biofilms, and (4) phytoremediation.

The suitability of phytoextraction methods is rather limited because the SPTF value for Cr is relatively low and varied for herbaceous plants from 0.1 to 0.6, and Cr is known to be concentrated mainly in roots (Bylińska, 1993). The addition of organic ligands (e.g., picolinic acid) can promote the phytoavailability of Cr, as Simon et al. (2001) reported for a fodder radish. Some other plant species (e.g., Cruciferae, *Salix*) also are proposed for the phytoremediation (Dheri et al., 2007; Quaggiotti et al., 2007).

The immobility of soil Cr may be responsible for an inadequate Cr supply to plants. Cr is of nutritional importance because it is a required element in human and animal nutrition. However, as Cary et al.¹²² stated, the Cr added to soil appeared to be very inefficient in terms of its recovery by food crops, although it caused an increase of this element in various plants.

Readily soluble Cr^{6+} in soils is toxic to plants and animals. Therefore, the variability in the oxidation states of Cr in soils is of great environmental concern. Pacha et al.¹¹¹ reported harmful effects also of Cr^{3+} compounds on the biochemical activity of soils. The sensitivity of soil enzymes differs, the highest being for dehydrogenase (Figure 11.4).

C PLANTS

There is no evidence to date of an essential role of Cr in plant metabolism. Described by Mertz⁵³⁴ positive effects on plant growth of Cr applications to soils having at low soluble Cr content may be artifacts.

Chromium is slightly available to plants and not easily translocated within plants, thus it is concentrated mainly in roots, apparently because of the propensity of Cr^{3+} to bind to cell walls (Zayed et al.,¹⁵⁷⁰). The most available to plants is Cr^{6+} , which is the very unstable form under normal soil conditions and its availability depends on soils properties, and especially on soil texture and pH. Also Cr^{3+} and several complex Cr anions (e.g., CrO_4^{2-}) may be easily available to plants. Zayed et al.,¹⁵⁷⁰ have shown that the patterns of accumulation and translocation of these two Cr species (Cr^{3+} and CrO_4^{2-}) are identical, however, Cr^{3+} is rather benign to most plants and binds strongly to soil solids. Application of farm yard manure (FYM) declines the Cr mobility (DTA-extractability) and thus mitigates effects of Cr toxicity in plants (Singh et al., 2007).

The mechanism of absorption and translocation of Cr in plants is apparently similar to those of Fe, and therefore the capability of roots to convert Cr^{3+} to CrO_4^{2-} is the key process in Cr absorption. This Cr conversion has been observed in spite of the different forms of Cr supplied to plants. There is some evidence that easily available Cr^{6+} is transformed into Cr^{3+} form in plant cells which readily interact with DNA and protein compounds (Zayed and Terry, 2003). Fendorf et al. (2004) concluded that Cr bioaccessibility is a function of soil type and retention time. These authors reported that patterns of accumulation and translocation of the two Cr ions (Cr^{3+} and CrO_4^{2-}) are rather identical. There is a great difference, however, in the accumulation of Cr by shoots and roots of various vegetable crops; the ratio shoot/root varies widely from 0.005 to 0.027. The highest concentration of Cr, supplied in two forms (Cr^{3+} and Cr^{6+}), was found in roots of plants of the Brassicaceae family, and the lowest in roots of *Allium* sp. Tiffin⁷⁸⁹ concluded that Cr is transported in plants as anionic complexes which have been identified in the extract of plant tissues and in xylem fluid. The presence of trioxalatochromate in plant leaves was reported.⁷⁹⁸ Pacha and Galimska-Stypa¹¹¹⁰ reported that Cr^{6+} compounds exhibit a strong mutagenic impact on *Bacillus subtilis* cells, while treatment with the Cr^{3+} compounds reveal slight mutagenic activities.

Contents of Cr in plants have recently received much attention due to the knowledge of its importance as an essential micronutrient in human metabolic processes, but also because of its carcinogenic effects. Thus, an adequate rate of nutritional Cr has become an important issue. Contents of Cr in cereal grains average from 0.01 mg/kg in wheat grains to 0.09 in oat grains (Table 11.3). Relatively high contents of Cr are in carrot (0.13 mg/kg), onion (0.16 mg/kg), and cabbage (0.13 mg/kg). Leafy vegetables and fruits contain Cr in the range of 0.04–0.08 mg/kg. Higher amounts of Cr are found in nuts (0.16 mg/kg) and almonds (0.11 mg/kg). The ranges of average contents of Cr in the mushroom, bay bolete (*Xerocomus badius*), sampled in the period of 1993–1998, from the northern part of Poland, were 0.22–0.75 and 0.20–0.71 mg/kg, in caps and stalks, respectively (Malinowska et al., 2004).

Contents of Cr in plants are controlled mainly by the soluble Cr contents of the soils (Figure 11.5). Most soils contain significant amounts of Cr, but its availability to plants is highly limited. However, the addition of Cr to soil affects the Cr content of plants, and the rate of Cr uptake by plants is dependent on various soil and plant factors. Several native plants, mainly those from areas of serpentine or chromite deposits, can accumulate Cr as much as 0.3% or 3.4% (AW).^{535,613}

Although stimulating effects of Cr on plants have been observed by several authors, the phytotoxicity of Cr has been often reported, especially in plants on contaminated soils or developed from ultrabasic rocks. There is some evidence of Cr phytotoxicity, and Chatterjee and Chatterjee (2000) reported that an excess of Cr in plants caused poor protein formation resulting from the disruption of the N metabolism. Increased level of Cr^{6+} in nutrient solution decreased CO_2 assimilation and other parameters associated with the photosystem of *Lolium perenne* leaves (Vernay et al., 2007). Schiavon et al. (2008) noticed the significant decrease of the S uptake rates by plants under the Cr-stress. Toxic effects of the Cr excess on germination of spinach plants depend on soil texture; in sandy soil it was at 40 mg Cr/kg, and in silty clay loam soils at 320 mg Cr/kg (Sharma et al., 2005). The elevated Cr content of soils is known to be responsible for the poor growth of forest trees.⁸⁵⁵

A highly increased accumulation of Cr in roots (up to 160 mg/kg), especially of Indian mustard and fodder radish, was observed in plants growing in Cr-polluted soil (247 mg/kg Cr) in the vicinity of a former galvanization plant.¹⁴⁹³ The Cr concentration in shoots of those plants did not exceed 10 mg/kg. Gough and Severson²⁷⁸ found Cr contents up to 500 mg/kg (AW) in sagebrush from the vicinity of a P fertilizer factory. Vegetables grown in allotment gardens near the oil refinery in Plock (Poland) have elevated concentrations of Cr, the maximum contents are (in mg/kg): carrot roots, 13; carrot leaves, 148; red beet roots, 6; and leaves, 154.¹⁴¹⁸

Anderson et al.²³ reported toxicity in oats having a Cr content of 49 mg/kg that where grown on soil containing 634 mg/kg Cr. Turner and Rust⁸¹⁰ observed initial symptoms of Cr toxicity with the addition of as little as 0.5 mg/kg Cr to the nutrient culture, and 60 mg/kg to the soil

TABLE 11.3
Chromium in Plants^a (μg/kg)

Plant	Range	Mean
Wheat, grains	4–0.20	10
Barley, grains	10–20	20
Oats, grains	40–600	90
Rye, grain	40–90	60
Carrots	50–210	130
Onion, bulbs	20–240	160
Maize (corn), cobs	220–290	—
Cabbaged	50–210	130
Potatoes, unpeeled	20–50	40
Legumes	500–160	90
Lettuces	30–60	50
Spinach	69–110	80
Cucumber	60–90	70
Tomato, fruits	70–130	90
Apple, fruits	10–100	80
Lemon, fruits	30–50	40
Hazelnuts	90–240	160
Almonds	80–150	110
Grass	500–3400	1100
Clover	200–4200	—

^a Compiled from ATSDR. 2002. *Draft toxicological profile for several trace elements*. U.S. Dept. Health & Human Services. Agency for Toxic Substances and Disease Registry, Atlanta, GA; Bratakos M.S., Lazos E.S., Bratakos S.M. 2002. *Sci Total Environ*, 290:47–58. Czekala, J., Chromium in Soils and Plants—Occurrence, Sorption and Uptake in Relation to its Fractions, Ph.D. dissertation, AR, Poznań, 274, 90, 1997 (Po); and Eriksson J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm.

culture. These Cr additions resulted in decreased concentrations of almost all major nutrients in tops and of K, P, Fe, and Mg in roots. The antagonistic interaction between Cr and Mn, Cu, and B has also been reported by Turner and Rust,⁸¹⁰ and this can be related to interferences both within the soil medium and in the plant tissues. In some cases, however, synergistic interactions between Cr and some elements (Ca, Mg, Fe, Mn, Cu) were also observed (Dong et al., 2007; Verany et al., 2007).

The toxicity of Cr depends on its oxidation state, but is also related to readily available forms of chromate. While a Cr₂O₇ addition at the 10^{−5} N concentration level decreased plant growth by about 25%, the same level of Cr₂(SO₄)₃ was without any effect on the growth, but the Cr additions resulted in the increase of Cr contents, to 2.2 and 1.3 mg/kg, respectively, in bush bean leaves.⁸⁴¹ The phytotoxic concentrations of Cr in tops of plants were reported as follows (in mg/kg): 18 to 24 in tobacco; 4 to 8 in corn; 10 mg/kg in barley seedlings; and 10 to 100.^{171,279,395} Kloke et al.¹⁰⁵² estimated that a very low Cr content, 1 to 2 mg/kg, inhibits the growth of sensitive plant species. The toxic levels of Cr reported by Macnicol and Beckett¹⁰⁸¹ are much broader and range from 1 to 10 mg/kg. At the same dose (750 mg/g soil) of Cr⁶⁺ and Cr³⁺, an increased uptake of Cr and reduced oat yield was observed, however, harmful effects were significantly greater in the case of Cr⁶⁺ addition.¹⁴⁰⁵ Dong

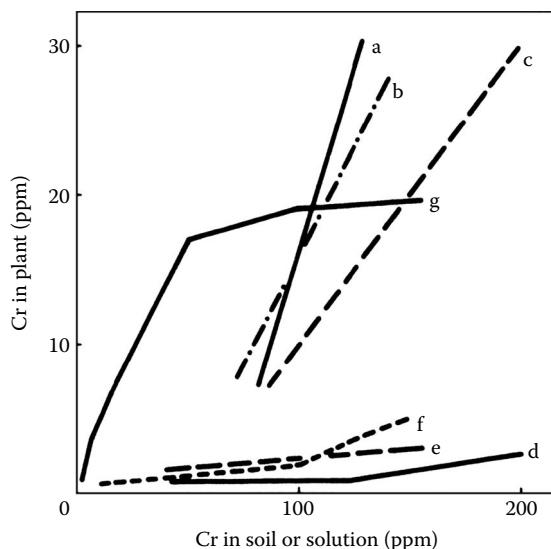


FIGURE 11.5 Concentration of Cr in plant tissues as a function of Cr content of soil. (a) potato stalks; (b) corn leaves; (c) wheat straw; (d) wheat grains; (e) barley grains; (f) tomato tops; and (g) tomato roots. (Data compiled from Cary, E. E., Allaway, W. H., and Olson, O. E., *J. Agric. Food Chem.*, 25, I, 300; II, 305, 1977; Diez, Th. and Rosopulo, A., *Sonderdruck Landw. Forsch.*, 33, 236, 1976.)

et al. (2007) observed that plants grown in Cr-contaminated soil may develop a Cr-tolerance resulted in increased activities of superoxide dismutase (SOD) and peroxidase (POD).

Symptoms of Cr toxicity appear as wilting of tops and root injury; also, chlorosis in young leaves, chlorotic bands on cereals, and brownish-red leaves are typical features. Increased levels of Cr in the nutrient solution (up to 10^4 μM) are reported to disorganize the fine structure of chloroplasts and the chloroplast membranes of *Lemna minor* (duckweed).⁵³

Chromium contents in moss samples from Norway, collected during the period 1990–1995, averaged 2.6 mg/kg, in the range of 0.21–290 mg/kg, across all samplings sites (Berg and Steinnes¹²²³). Lichens from the Wisconsin State, United States sampled during the period 1987–2001 contained Cr at the average value of 1.2 mg/kg, in the range from 1.1 to 1.4 mg/kg (Bennett and Wetmore, 2003). Kitagishi and Yamane³⁹⁵ gave a range of Cr in lichens collected within urban areas to be 5–10 mg/kg. Folkesson²³⁹ found 5 mg/kg Cr in mosses near peat-fired plants and 9 mg/kg Cr in mosses from the edge of a waste heap of ash, as contrasted with background concentrations of 1–1.5 mg/kg. These data indicated a rather stable emission of Cr to the atmosphere in these regions.

II MOLYBDENUM

A INTRODUCTION

The average content of Mo is given for the upper Earth's crust as 1.5 mg/kg (Table 3.2) and its concentration is elevated in granitic rocks and argillaceous sediments, up to 2.5 mg/kg (Table 11.2).

Molybdenum has various oxidation states (Table 11.1) and exhibits unusual geochemical behavior since in most environmental compartments it is likely to form oxyanions, however, under reducing conditions it has a high affinity for sulfur. The most common Mo mineral is molybdenite, MoS_2 , which occurs in several geological formations. Less frequent are: molibdite, MoO_3 ; wulfenite, PbMoO_4 ; and powellite, CaMoO_4 . Several other Mo minerals, mainly oxides, are known to be associated with various sediments and often are associated with Fe and Ti minerals. Especially

Mn–Fe rich nodules have the ability to concentrate Mo up to 2000 mg/kg (Fairbridge, 1972). Ferromanganese oxides in ocean sediments are known to accumulate high amounts of Mo (Anbar, 2004). These concretions seem to occur under anoxic S-rich conditions (Arnold et al., 2004). Szefer (2002) gives the range of 20–507 mg/kg for Mo in ferromanganese nodules of the Baltic Sea. The Mo content in soil Mn-nodules is reported to reach 410 mg/kg (Kabata-Pendias and Sadurski, 2004). There is a close similarity in the behavior of Mo and W in the environment, and both are present mainly in anionic forms.

Molybdenite, a primary ore deposit, is a main source of Mo. By-products, generally from copper mines, are additional sources of Mo. Annual production of Mo in 2008 was 212 kt (USDI, 2009). Its main use is in metallurgy for the hardening of alloys. This metal is also widely used in electronics and chemistry (e.g., catalysts).

B SOILS

The world-soil average content of Mo in soils has been established as 1.1 mg/kg (range 0.9–1.8 mg/kg) and is fairly similar to its crustal abundance (Table 3.2). Mo behaves both like a chalcophile and a lithophile element, and in soil, in aerobic condition, occurs mainly as the molybdate oxyanion.

During weathering processes, Mo sulfides are slowly oxidized and yield mainly the Mo_4^{2-} anion which dominates in neutral and moderate alkaline pH ranges, and HMoO_4^- which occurs at lower pH values. However, easily mobile anions are readily coprecipitated by OM, CaCO_3 , and by several cations, such as Pb^{2+} , Cu^{2+} , Zn^{2+} , Mn^{2+} , and Ca^{2+} . Also, differential adsorption of Mo by Fe, Al, and Mn hydrous oxides contributes to the retention of Mo in surface deposits. Mo species may be bound to Fe and Al oxides in soils and sediments, what may determine its behavior in the environment. Mo association with OM also controls its mobility. All these reactions are highly dependent on pH and Eh conditions and therefore the net results of Mo migration during weathering may be poorly predictable.

The Mo content of soils usually resembles that of their parent rocks, and do not differ much among various soil groups (Table 11.2). The Mo means for different soil units vary from 1.3 mg/kg for sandy podzols to 2.8 mg/kg for loamy cambisols. The 90th percentile value for Mo in Finnish soils is 1.5 mg/kg (Köljonen¹³⁶⁸), whereas the median content of Mo in Lithuanian soils is reported to be 0.62 mg/kg and does not show any distinct association with soil texture (Kadunas et al.¹³⁵⁹). Swedish arable soils contain Mo in the range from 0.1 to 4 mg/kg, at an average value of 0.6 mg/kg (Eriksson, 2001). Govindaraju¹³¹³ presented the results for Mo in reference soils from China to range from 0.3 to 18 mg/kg, and in soils from the United States in the range 1–2 mg/kg. Kubota⁴³⁵ estimated the range of Mo in U.S. soils from 0.08 to over 30 mg/kg and the median concentration as slightly more than 1 mg/kg. A very high content of Mo, up to 24 mg/kg, is reported to be in soils of British Columbia (Canada) where commercial production of vegetables takes place.¹⁴⁵³

The behavior of Mo in soils has been extensively studied because it has a rather unique position among other micronutrients in that it is least soluble in acid soils and readily mobilized in alkaline soils (Figure 11.6). Vlek and Lindsay⁸²⁷ and Lindsay⁴⁷⁷ studied the behavior of different Mo minerals and concluded that soil solubility of Mo is very close to that of PbMoO_4 in soils. This mineral (wulfenite), however, cannot be expected to be the most common Mo compound in soil. It seems most likely that a great proportion of soil Mo is associated with matter and Fe hydrous oxides. This is supported by findings of Cumakov,⁹⁷³ who studied the Mo speciation in various soils. He found the highest proportion of Mo to be associated with polymeric organic compounds resistant to oxidation processes. Other kinds of organic substances also reveal a higher affinity to Mo than clay minerals (Table 11.4). Due to the great affinity of Mo to be fixed by OM, its concentration in forest litter can reach 50 mg/kg.

Kraushkopf,⁴²⁷ Norrish,⁵⁷⁰ and Lindsay⁴⁷⁷ reviewed findings on Mo behavior in soils and concluded that, in the inorganic forms, Mo is associated mainly with Fe oxides, probably as an adsorbed phase. The molybdate adsorbed on freshly precipitated $\text{Fe}(\text{OH})_3$ is readily exchangeable; but as the

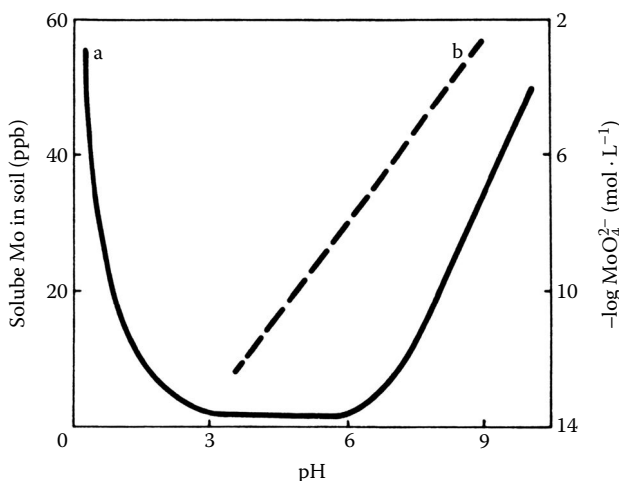


FIGURE 11.6 Solubility* of Mo (a) and activity of Mo (b) as a function of soil pH. *Soil containing 1.6 mg/kg Mo leached with HCl and KOH in the presence of 1 mM CaCl_2 . (Data compiled from Karlsson, N., *Statens Lantbrukskem, Kontrollanst. Medd.*, 23, 243, 1961 (Sv); Lindsay, W. L., *Micronutrients in Agriculture*, Soil Science Society of America, Madison, WI, 41, 1972a.)

precipitate ages the Mo becomes less soluble and ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$) or other slightly soluble Fe–Mo semicrystalline forms may occur.

The mobility, and thus availability of Mo to plants, is highly governed by soil pH and drainage conditions. Mo from wet alkaline soils is most easily taken up, but the geochemical processes involved in this phenomenon are not completely understood. Apparently, this uptake is related to the high activity of MoO_4^{2-} in an alkaline medium (Figure 11.6), as well as to an ability to form soluble thiomolybdates under reducing conditions (e.g., MoS_4^{2-} , $\text{MoO}_2\text{S}_2^{2-}$). Lindsay⁴⁷⁷ assumed that plants

TABLE 11.4
Molybdenum Species in Soils (Mean Values for Chernozems and Fluvigleysols)

Species	Content of Mo Species	
	mg/kg	% of Total Mo
H_2O soluble	0.097	3.5
Fixed on clay surface	0.269	9.8
Fixed by organic substances occluding sesquioxides	0.455	16.8
Fixed by organic substances (only)	0.439	16.2
Fixed by polymeric organic compounds resistant to oxidation	0.846	31.3
Fixed by inorganic C-particles	0.150	5.6
Residual	0.458	16.8

Source: Data from Cumakov, A., Trace Elements in Slovakian Soils and Plant Nutrition, Ph.D. thesis, Institute of Sugar Industry, Bratislava, 350, 1988 (Cz).

growing in a reducing environment are capable of transporting O_2 through the stem to the roots, and therefore Mo compounds close to the root surface become more oxidized and thus more soluble. The impact of sewage sludge on the mobility and phytoavailability of Mo has been observed.¹³⁵⁷

On acid soils ($pH < 5.5$) low in Mo, and especially on those with a high Fe oxide level, Mo is hardly available to plants. The low availability of Mo that occasionally appears in peat soils seems to be affected by strong fixation of Mo^{5+} by HA following the earlier reduction of the MoO_4^{2-} , as stated by Mengel and Kirby.⁵³¹ On the contrary, organic-rich soils can supply adequate amounts of Mo to plants due to a slow release of this element from organic bond forms.

Liming of acid soils is a common practice to increase the Mo availability to plants. However, at higher rates of liming, the solubility of Mo may decrease due to its adsorption by $CaCO_3$.⁷⁷² The application of Mo salts also increases the available Mo pool in soils, and it is preferable to liming when an increase in soil pH is not desired. Great caution must be taken in Mo fertilization, as this can result in high Mo levels in fodder. Ammonium oxalate solution is currently used to extract the available Mo from soil, as well as hot water leaching.¹⁵¹

Soils in arid and semiarid regions, especially ferrasols, generally have higher Mo contents. However, in humid and temperate regions, soils over Mo-rich material may also contain hazardous amounts of Mo. These soils and soils polluted with Mo, need amelioration to depress the Mo availability to plants. The application of S is most effective, whereas increasing P level in soils is known to stimulate Mo uptake by plants.

Industrial pollution (mining, smelting, processing of metals, and oil refining) may be responsible for elevated Mo concentrations in soils. Soils in arid and semiarid regions, especially ferrasols, usually contain relatively high amounts of Mo. These soils and soil contaminated with Mo, need amelioration to depress the Mo availability to plants. Increased contents of Mo, up to 35 mg/kg are reported for the vicinity of Mo processing plants in the United States, and up to 38 mg/kg (range of 22.2–38.2) in Chile (Hornick et al.,³²⁴ Schalscha et al.¹¹³⁹).

Some sewage sludges contain elevated amounts of Mo (up to 50 mg/kg) and may have an impact on both enriching the total Mo content and increasing the solubility of soil Mo.^{314,452} Also, fallout or the application of fly-ash from some coal-fired power plants should be considered as potential sources of Mo, since even if only small amounts of Mo are added, its availability is increased by the alkaline reaction of fly-ashes. Mo is also frequently found in sludges (at average concentration of 40 mg/kg),¹¹¹⁶ in forms easily available to plants. Where Mo-enriched sludges are destined for application to land, crops should be monitored to ensure that Mo concentrations are within safe limits, especially for grazing animals.

C PLANTS

1 Absorption and Biochemical Functions

Mo is an essential micronutrient, but the physiological requirement for this element is relatively low. Its mobility and phytoavailability increases with soil pH. Sardans et al. (2008) observed that drought affects the Mo uptake by plants and depending on plant species its concentration may increase or decrease.

Plants take up Mo mainly as molybdate ions, and its absorption is proportional to its concentration in the soil solution. Although there is no direct evidence, there is a suggestion of the active uptake of Mo.⁵⁴⁸ Mo is moderately mobile in plants, but forms of translocated Mo are unknown. Tiffin⁷⁸⁸ discussed the possibility of organic complexing, mainly of the Mo–S amino acid complex that was found in the xylem fluid. Some proteins are involved in the transport of molybdate in plants (Dudev and Lim, 2004). Tomatsu et al. (2007) identified the protein (MOT1) as the transporter of Mo within plant cells, and Fitri et al. (2008) reported that two Mo-bound species to proteins/polypeptides occur in raw phloem sap of bean.

Molybdenum is the essential component of several enzymes, such as nitrate reductase, xanthine dehydrogenase, aldehyde oxidase, and sulfide oxidase, and possible enzymes (oxidases) that catalyze

diverse and unrelated reactions (Kaiser et al., 2005; Stroumin and Vunkova-Radeva, 2007). The basic enzymatic role of Mo is related to its function as a redox carrier and is apparently reflected in the valency change between Mo^{6+} and Mo^{5+} .⁵⁶⁴ Ivchenko¹⁰³⁴ reviewed findings on Mo functions in the metabolism of plants and emphasized a high concentration of Mo in nucleic acids and its inhibitory and regulatory functions in enzymatic activities of DNA and RNA. In biochemical processes of some anaerobic organisms, a substitution of Mo by W in enzymes has been observed (Buc et al., 1999; Makdessi et al., 2001).

Normally, there is 1 mg/kg or less of Mo in leaf tissues, whereas nodulated roots contain several times these concentrations. Requirements for Mo are generally met at concentrations within the range of 0.2–5 mg/kg in tissues of most plants; only some leguminous crops require more Mo. Most of this Mo apparently is in the nitrate reductase of root and shoot and in the nitrogenase of the nodule bacterioids. Two Mo-containing enzymes in the N metabolism are involved in either N_2 fixation or NO_3 reduction. Thus, the requirement of plants for Mo appears to be related to the N supply; plants supplied with $\text{NH}_4\text{-N}$ have less need for Mo than those utilizing $\text{NH}_3\text{-N}$. Lopez et al. (2007) reported that the nitrogenase activity and number and weight of nodules of red clover increased significantly with increased available Mo in the soil.

Molybdenum is known to be essential to microorganisms, and some bacteria species are able to oxidize molybdenite in soils. Rhizobium bacteria and other N-fixing microorganisms have an especially large requirement for Mo. Some fungi and nitrogen-fixing bacteria tend to concentrate Mo up to 100 mg/kg.

Since the most important function of Mo in plants is NO_3 reduction, a deficiency of this micronutrient causes symptoms similar to those of N deficiency. Some plants, however, also show more specific Mo deficiency symptoms (e.g., “whiptail” in cauliflower) (Table 5.10). A deficient Mo content of plants depends on various factors, in particular, on interactions with other elements. Although easily soluble soil Mo is also readily taken up by plants and some plant species are known to accumulate much Mo, its toxicity symptoms in plants under field conditions are very rare, whereas toxicities to animals feeding on forages high in this element are well-known. The only relatively high concentration of Mo that was toxic, 135 mg/kg, was reported by Davis et al.¹⁷¹ for young spring barley.

Crop response, particularly of leguminous crops, to Mo application has been widely reported for soil conditions throughout the world, especially for acid and ferrallitic soils. While correction of Mo deficiencies may be accomplished by Mo application as soil, foliar, or seed treatments, care must be taken in its use since Mo may be very toxic, even at quite low concentrations, in fodder plants. The Mo-fuse with glass has also been proposed for controlling the Mo deficiency. However, the preferable control of Mo deficiency is liming the soil to a pH of around 6.5. The application of Mo fertilizers has to be based on a proper assessment of Mo doses and is the subject of several publications (Mortvedt et al., 1991; Pierzynski and Jacobs, 1986; Wang et al., 1994).

2 Interactions with Other Elements

Several complex interactions between Mo and other elements are observed within plant tissues and also in the external root media (Figure 5.8). The most important interactions are those between Cu, Mo, and S, which are differentially governed by diverse factors.

The Mo–Cu antagonism in plants is strongly related to N metabolism. The Mo–S relations may have antagonistic or stimulative effects on Mo uptake by plants, depending on the rate of application of S-containing fertilizers.⁵⁸¹ However, a wide range of combinations between Cu, Mo, and S in herbage and, further, in animal nutrition, may occur. Gartrell²⁵⁷ has reviewed this topic and made a few generalizations showing that soil factors that increase the availability of Mo to plants usually have inhibitory effects on the Cu uptake by plants and that the physiological barrier to Mo uptake by plants is much less effective than that to Cu uptake. Nutritional effects of Cu:Mo ratios in pastures on animal health is controlled by the sulfate concentration in plants, and an increased level of SO_4^{2-} may reduce Cu absorption with even small amounts of Mo. It has been established that soils

with 5 mg/kg Mo can be associated with growth retardation and lower reproduction in cattle due to the Mo–Cu nutritional relationship.

Mo–Mn antagonism resulting from soil acidity influences the availability of these elements; therefore, liming can correct both Mo deficiency and Mn toxicity. Mo–Fe interactions are demonstrated as low Mo availability in Fe-rich soils, whereas increased Mo levels may induce Fe deficiency, or accentuated Mn-induced Fe chlorosis. Although mechanisms of the various interactions are not well-understood, the formation of Fe–Mo precipitates within root tissues may be responsible for low a Mo translocation.⁵⁸¹

Mo–W and Mo–V metabolic interactions are not precluded, since a substitution is possible between these elements in biochemical processes. A Mo–P interaction is often demonstrated as an enhancing effect of P on Mo availability in acid soils, apparently due to both a higher solubility of the phosphomolybdate complex, as well as to a higher Mo mobility within plant tissues. However, reported effects of P fertilizers on Mo availability are contradictory, and while the ordinary SO_4^{2-} containing superphosphate reduced Mo uptake, concentrated superphosphate increased Mo uptake.³ Thus, Mo–P interactions are variable and highly governed by diverse soil factors and are also related to plant metabolic processes. Mo–Ca interactions are complex and highly cross-linked with the range of the soil pH.

3 Concentrations in Plants

No simple relationship is apparent between the total Mo contents of soils and plants, although some authors have reported a linear relationship for Mo content of herbage and its total concentration in soil. The Mo concentrations in plants closely reflect the mobile Mo pool, for Mo seems to be very readily absorbed by plants when present in soluble forms. The Mo uptake by plants is a function of soil pH (Figure 11.7). Usually a positive correlation is observed between the relative Mo uptake and the soil pH. This has been clearly demonstrated by Doyle et al.,¹⁹³ who found abnormally high Mo values (up to 52, and mean 11 mg/kg) in native plants grown on neutral or alkaline soils, whereas on Mo-rich acid soils, and Mo-low soils, Mo concentrations in the same varieties of plants averaged respectively, 0.9 and 0.2 mg/kg.

Some native plants, particularly leguminous species, are known to accumulate as much as about 500 mg/kg (AW) Mo, or about 350 mg/kg, without showing toxicity symptoms.^{556,618} The Mo content

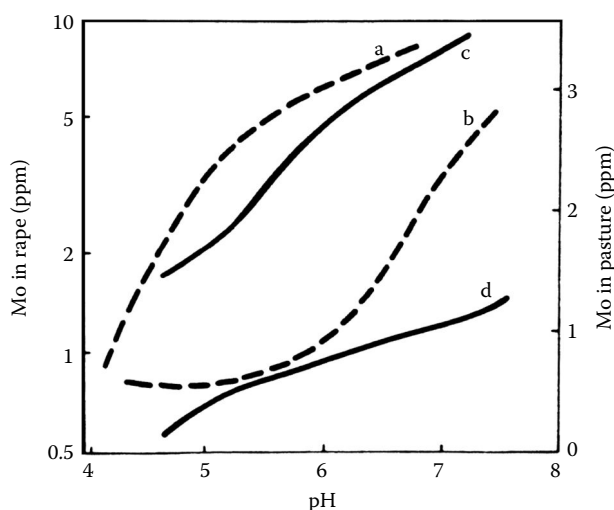


FIGURE 11.7 The effect of soil pH on the Mo content of (a) pasture on peat bog soil; (b) pasture on mineral soil; (c) rape, shoots; and (d) rape, roots. (Data compiled from Gorchach, E. and Gorchach, K., *Acta Agrar. Silvestria*, 16, 20, 1976 (Po); Karlsson, N., *Statens Lantbrukskem, Kontrollanst. Medd.*, 23, 243, 1961 (Sv).)

of forages is of special concern; therefore, most available data are on the Mo status in grasses and legumes. Mean Mo levels range from 0.33 to 1.5 mg/kg in grasses and from 0.73 to 2.3 mg/kg in legumes from different countries. In areas where Mo toxicity was observed in grazing animals, the Mo content of grasses ranged from 1.5 to 5.0 mg/kg, and in legumes from 5.2 to 26.6 mg/kg (Tables 11.5 and 11.6). In general, Mo levels greater than 10 mg/kg in forage present a serious problem to most classes of livestock. In pasture, Mo is known to vary with different stages of plant development and with periods of the growing season. The reported Mo content was high in the spring and autumn seasons.³⁸⁴ Phillips and Meyer^{1117a} observed a decrease in Mo concentrations of alfalfa from fields known for high Mo levels, during the period from 1950 to 1985. The decline in Mo average contents from 10.78 to 3.57 mg/kg is, according to these authors, caused by leaching of soluble salts with irrigation, acidification of soils by N fertilizers, and crop removal.

Plant foodstuffs contain variable amounts of Mo within the range of 0.07–1.75 mg/kg, with legume vegetables being in the upper range and fruits being in the lower range (Table 11.7). The Mo contents of cereal grains averages 0.49 mg/kg and does not show a great variation under widely ranging field conditions in various countries. The ranges of average values for Mo contents in cereal grains reported by different authors are as follows (mg/kg): wheat, 0.18–0.64; rye, 0.4–0.54; barley, 0.16–0.72; and oats, 0.41–0.88. Brüggemann et al.¹²⁴⁷ presented Mo concentrations in plant foodstuffs, collected in Germany during the period 1989 to 1994, as follows (mg/kg): rye grain, 0.539; wheat grain, 0.394; potato (unpeeled tubers), 0.21; and dehydrated potato, 0.007. The concentration of Mo in grass is of great concern, since grazing cattle can suffer from Mo toxicity, especially when there is a low content of Cu (ratio Cu:Mo below 4 to 5) and low S supply in forage.

The ready availability of Mo causes a great increase in its uptake when plants are grown in contaminated sites. Karlsson³⁸⁴ found up to 200 mg/kg of Mo in pasture plants from the vicinity of

TABLE 11.5
Molybdenum Content of Grasses and Legumes from Areas Where Mo Toxicity in Grazing Animals Was Not Observed (mg/kg)

Country	Grasses		Legumes		Reference
	Range	Mean	Range	Mean	
Bulgaria	—	—	0.04–0.32	0.18	220
Canada	0.4–8.0	1.3	—	—	192
Czech Republic	—	0.3	—	—	154
Finland	0.14–0.80	0.38 ^a	—	—	221
	0.23–0.91	0.45	0.20–1.3	0.70	591; 727
Germany	0.08–1.04	0.33	0.21–5.0	0.80	31; 65
Germany	0.42–0.88	0.70	—	—	596
Great Britain	0.5–4.0 ^b	—	—	—	784
	0.25–1.47	0.56	—	—	543
Ireland	0.18–0.77	—	0.28–0.52	—	235
Japan	0.04–3.05	0.72	0.01–3.64	0.92	770
Poland	<0.02–1.68	0.33	0.02–3.56	0.50	1045
Sweden	0.2–4.8	1.4	0.3–20.5	2.5	384
U.S. ^c	0.5–2.0	—	<0.7–15.0	1.8	710
U.S.	—	—	0.01–3.46	0.73	435
Russia	—	—	1.31–3.61	2.3	337

^a Grass heavily fertilized with N.

^b Pasture herbage.

^c Calculated from AW basis.

TABLE 11.6
Molybdenum Content of Forage Plants from Areas where Mo
Toxicity in Grazing Animals was Observed (mg/kg)

Country	Grasses		Legumes		Reference
	Range	Mean	Range	Mean	
Canada	0.6–17.0	4.0	1.0–20.0	5.2	192
	2.4–12.0	5.0 ^a	4.8–6.0	5.4 ^a	237
Great Britain	0.1–7.2	1.5 ^b	—	—	784
Sweden	1–234 ^b	—	—	—	384
U.S.	0.7–6.8	3.7	19–40	26.6	434
Russia	10–50 ^b	—	—	—	420

^a Samples from the periphery of a Mo ore body.

^b Pasture herbage.

a metallurgical factory. Hornick et al.³²⁴ reported that plants grown in the Mo-polluted soil near a Mo processing plant accumulated this element in concentrations ranging from 124 to 1061 mg/kg in lettuce and cabbage, respectively. Furr et al.²⁵⁰ found that beans and cabbage grown in soil amended with municipal sludge ashes had an increased Mo content up to 18 and 19 mg/kg contrasted to the control values of 0.8 and 0.4 mg/kg, respectively. Grasses grown in the vicinity of a Mo ore-processing plant in Chile contain as much as 6.5–36.0 mg/kg.¹¹³⁹ Thus, elevated Mo concentration in soils resulting from industrial pollution or agricultural practices may be locally responsible for the pronounced abnormal Mo content of plants.

TABLE 11.7
Molybdenum Content of Plant Foodstuffs (mg/kg)

Plant	Tissue Sample	FW Basis	DW Basis	AW Basis
		(574, 705, 1187)	(337, 589, 705, 910)	(705)
Sweet corn	Grains	0.045; 0.22	0.18	6.9
Kidney bean	Seeds	—	0.9–1.6	—
Pea	Seeds	—	1.2–1.75	—
Snap bean	Pods	0.23	2.1	30.0
Carrot	Roots	<0.08; 0.015	0.04	7.0
Sugar beet	Roots	—	0.45–0.75	—
	Leaves	—	0.39	—
Lettuce	Leaves	0.005	0.074	0.53
Cabbage	Leaves	<0.099	0.85	9.1
Potato	Tubers	0.047	0.25, 0.15	5.9
Onion	Bulbs	0.024; 0.016	0.24, 0.16	5.6
Cucumber	Fruits	<0.087	0.82	8.3
Tomato	Fruits	0.042; 0.024	0.82	6.8
Apple	Fruits	0.0018	0.07	3.9
Orange	Fruits	0.014	0.11	3.1
Tea	Leaves	—	0.2–0.3	—

Note: References are given within parentheses.

In mosses sampled in Norway in the period 1990–1995, amounts of Mo varied from <0.006 to 11 mg/kg (Berg and Steinnes¹²²³). Concentrations of Mo in mosses from Germany ranged from 0.05 to 5.5 mg/kg (Reimann and de Caritat, 1998).

III TUNGSTEN

A INTRODUCTION

Concentrations of W in the Earth's crust average 1.5 mg/kg (Table 3.2) and increase in acid igneous rocks and argillaceous sediments (Table 11.2). The common concentration of W in granite rocks and argillaceous sediments varies from 1 to 2 mg/kg, and in mafic rocks and in limestones, from 0.5 to 1 mg/kg. Its content in coals is relatively high and averages 0.5–1 mg/kg, and in some oil shales can reach up to 2.5 mg/kg (Li, 2000). In fly-ash samples from coal-fired power plant in Indiana (the United States), contents of W vary in the range of 1.04–1.17 mg/kg (Brake et al., 2004).

Geochemical properties of W are similar to those of Mo and in several minerals the substitution of W for Mo is observed. Predominate minerals contain the anionic form of the metal, $(\text{WO}_4)^{2-}$. The common minerals are wolframite, $(\text{Fe}, \text{Mn})(\text{WO}_4)$; sanmartine, $(\text{Zn}, \text{Fe})(\text{WO}_4)$; and scheelite, CaWO_4 . However, several tungstanites, anhydrous and hydrous, in coordination with different metals are known. Under most geochemical conditions, minerals and compounds of W are slightly soluble, but some complex compounds, especially those associated with Mo are likely to be mobilized under specific conditions. In the environment, W is mainly present in anionic form, tungstate (WO_4^{2-}) , as well as in protonated and polymerized species. Under reducing conditions (for example in the bottom sediments), other species may form because of the reduction of W to lower valence states.

Global production of W was estimated as 54.6 kt in 2008 (USDI, 2009). It is usually mined from scheelite or wolframite. W is an important strategic metal that is used in a variety of industrial applications, mainly in metallurgy as an addition to alloys for abrasives and cutting tools. W is broadly utilized for rocket engines, x-ray tubes and various electric tools, and in the lighting industry (e.g., light bulbs). It is also used for catalysts in automobile exhaust systems, and as pigments in dyes and inks. W carbide (WC) has a hardness of that of diamond.

Tungsten is released to the environment, for example, through its use in winter tires and ammunition. Its other sources are not well known.

B SOILS

The average W contents in worldwide soils is estimated as 1.7 mg/kg, within the range of <0.17 – <5.0 (Table 3.2). The highest mean W content (<5.0 mg/kg) is reported for soil of Europe (FOREGS, 2005), however, data are not referred to soil groups. Elevated W levels are observed in loamy soils (Table 11.2). Ure et al.⁸¹⁹ found a range of W from 0.68 to 2.7 mg/kg in Scottish soils derived from different parent material, with the highest value for soil over quartz-mica schist and the lowest in the soil over serpentine. In the reference soils from China W contents range from 0.95 to 85.5 mg/kg, and in soils from the United States from 0.5 to 5 mg/kg.¹³¹³ The soils of Finland contain 2.23 mg/kg W at the 90th percentile range.¹³⁶⁸ Agricultural soils of Sweden contain W from 0.4 to 2.4 mg/kg (Eriksson, 2001). Takeda et al. (2004) gave the W range as 0.9 – 1.8 mg/kg in agricultural soils of Japan. Data presented by Čurlík and Šefčík (1999) indicate that W levels <1 mg/kg predominate in soils of the Slovak Republic, and only locally increased contents, up to 51 mg/kg, was noticed.

Panova¹¹¹⁵ described W species in polluted soils surrounding a W ore-processing plant in the former Soviet Union. The total W contents of these soils varied from 100 to 2000 mg/kg, of which 50% was present in the forms of primary minerals, 30% was H_2O soluble, 15% was bound to Fe oxides, and 5% was associated with HA and FA. Furr et al.²⁵⁰ reported W contents in two sludge ashes of (the United States) as 43 and 186 mg/kg.

Braida et al. (2007) emphasized a need of studies on the W behavior in soil and on remediation since the use of W in new types of ammunition is increasing what elevates its input into the environment.

C PLANTS

Apparently, like Mo, W is easily available to plants under certain conditions. Wilson and Cline⁸⁸² found that barley grown in soils with added ¹⁸⁵W removed a large proportion of that radionuclide and that the lower uptake from acid soil suggested that plants probably take up an anionic form, WO_4^{2-} . Also Bell and Sneed⁶² reported a high accumulation, in plant roots, of this radionuclide, that is released from nuclear reactions. W is likely to be elevated in plants growing on soil overlying W ore bodies and is used in geochemical prospecting for sheelite-bearing ore-bodies (Quin and Brooks, 1974). Plants growing in a mineralized zone contained up to 18 times the background W value of 2.7 mg/kg without showing toxicity symptoms.²⁷⁹

There is no clear evidence that W might have a biological function in plants. Makdessi et al. (2001) reported that the function of W, as a component of two dehydrogenases of some bacteria (e.g., *Eubacterium acidaminophilum*), has now been fully recognized. It probably displays competitive inhibition of Mo in the enzyme nitrate reductase, reducing catalytic activity of this enzyme (Pais and Jones¹⁴⁴⁸). Jiang et al. (2007) observed that W is a potential inhibitor of the ABA biosynthesis in plants in both conditions, in the greenhouse and in the field at a site naturally W-enriched. However, under drought stress, W may have an inhibitory effect on the ABA accumulation. Gough et al.²⁷⁹ reviewed the possible toxicity of W to plants, which appears to be moderate.

Behaviors of Mo and W are very similar in biochemical processes and some substitution by W for Mo has been reported (Buc et al., 1999; Makdessi et al., 2001; Tajima, 2005). There have been some observations on the antagonistic interactions between W and Mo causing a slower N-fixation process that is governed by pH of the media (Zajic⁸⁹⁸). Nicholas⁵⁶⁴ mentioned that when W is substituted for Mo in the nitrate reductase enzyme, it has no catalytic activity.

The common range of W in terrestrial plants is established at the range of <1–150 µg/kg, whereas Markert^{1399a} has proposed 200 µg/kg for W in the standard plant. Bowen⁹⁴ gave the overall range of W as 10–150 µg/kg in land plants. Connor and Shacklette¹⁴⁵ found the W range from 30 to 70 mg/kg (AW) of tree samples. Contents of W in vegetables vary within the range from <1 to 350 µg/kg (Duke¹⁹⁷). Wheat and barley grains from Sweden contain W at averages values of 6 and 5 µg/kg, respectively (Eriksson, 2001).

Furr et al.¹⁰⁰⁴ found W to range from 0.7 to 3.5 mg/kg in vegetables growing on soil amended with fly-ash. Panova¹¹¹⁵ studied W distribution in semiarid herb (mother wort) grown in a vicinity of the W industry and observed a linear decrease of W content, from 600 to 50 mg/kg (AW), with increasing distance from the pollution source.

In mosses sampled in Norway during 1990–1995, amounts of W varied from <2 to 1500 µg/kg (Berg and Steinnes¹²²³). Concentrations of W in mosses from Germany ranged from 10 to 2500 µg/kg (Reimann and de Caritat, 1998). Bowen⁹⁴ cited the W levels in lichens and bryophytes to range within 20–130 µg/kg.

12 Elements of Group 7 (Previously Group VIIb)

The Group 7 is composed of three elements: manganese (Mn), technetium (Tc), and rhenium (Re). Only Mn is essential to living organisms. Tc is a by-product of nuclear fuel processing and occurs as unstable radionuclides with variable but mainly short half-lives (from seconds to years). Re is highly dispersed in the environment. All elements of Group 7 have variable valences (Table 12.1) and reveal both lithophile and chalcophile characters.

I MANGANESE

A INTRODUCTION

Manganese is one of the most abundant among trace elements in the lithosphere (Table 3.2). Its common occurrence in rocks ranges from 350 to 2000 mg/kg and higher concentrations are associated with mafic rocks (Table 12.2).

Manganese is a member of the iron family and both elements are closely associated in geochemical processes. Thus, Mn cycles follow Fe cycles in various terrestrial environments. There are a number of Mn minerals, mainly in the association with other metals, and with Fe in particular. The most common “only Mn mineral” is pyrolusite, β - MnO_2 ; the others are: manganite, γ - MnOOH ; hausmannite (Mn_3O_4); and rodochroizite, MnCO_3 . Birnessite, $\text{Na}_x\text{Ca}_y\text{Mn}_7\text{O}_{14}(2.8\text{H}_2\text{O})$, of an unconfirmed composition, apparently associated with alkaline soils, occurs in groundwater and desert varnish, and exhibits a large adsorption capacity to some metals (Cd, Co, Cu, Pb, Zn) and oxidizing potential higher than other Mn minerals (Feng et al., 2007).

During weathering, Mn in minerals are oxidized under atmospheric conditions and released Mn oxides are reprecipitated and readily concentrated in forms of secondary Mn minerals, often as concretions and nodules. Under weathering in tropical and subtropical conditions, Mn is concentrated in residual deposits, while under humid colder climate, Mn is leached by acid solutions from sediments and soils. Complex behavior of Mn in geochemical processes resulted in the accumulation of this metal in different layers of sediments, in soil concretions (Table 4.3), and in deep-sea sediment polymetallic concretions.

The redox state of Mn is variable from +2 to +7 (Table 12.1) and is mediated by both geochemical and biological processes. Most common is the cation Mn^{2+} that readily replaces the sites of other divalent cations (e.g., Fe^{2+} , Mg^{2+}). The complex mineralogical and chemical behavior of Mn and its participation in reduction–oxidation processes resulted in the formation of a large number of oxides and hydroxides of variable stability and properties. The physical features of Mn compounds and minerals, especially small size of crystals and large surface areas of amorphous forms, have important geochemical and pedochemical implications. Manganese is highly associated with activities of microbes in both sediments and soils.

Mn oxides (as well as Fe oxides) are considered to be the most abundant compounds of the Earth’s surface that can serve as anaerobic terminal electron acceptors in microbial metabolism. According to Megoñigal et al. (2003) microorganisms play a key role in the Mn cycling. Tebo et al. (2003) have described the Mn-oxide biomineralization and the role of those Mn oxides in the transformation/ degradation of organic and inorganic compounds in various environmental compartments.

TABLE 12.1
Selected Properties of Trace Elements of Group 7

Element	Atomic Number	Atomic Mass	Atomic Radius (pm)	Density (20°C) (g/cm ³)	Valence ^c
Mn, manganese	25	54.9	179	7.44	+2 ^a
⁹⁸ Tc, technetium	43	98.9 ^b	—	11.5	+4, +6, +7
Re, rhenium	75	186.2	197	21.0	+7 ^c

^a Variable oxidation states from +2 to +7.

^b For the most stable isotope ⁹⁸Tc.

^c Variable oxidation states from −1 to +7.

Global annual production of Mn in 2008 was 14 Mt (USDI, 2009). The Mn ores are widely spread in various geological and climatic conditions and concentrated mainly in residual deposits, as various oxides and hydroxides; to a lesser extent as carbonates and silicates.

Manganese is used mainly in the metallurgical industry for steel and various alloys to provide hardness and toughness, and as antioxidant. Alloys with Mn are used in the electrical industry (e.g., dry-cell batteries). It is also broadly applied for the production of pigments, ceramics, and glass. Manganese sulfate, MnSO₄, is used as fertilizer and as livestock supplement. Mn compounds are relatively broadly used as fungicides, mainly for the seed treatment.

Since 1970, Mn has been used in gasoline, first in Canada and the United States, as an antiknock agent (as replacement for Pb in unleaded fuel), in a form of organic compound—methylocyclopentadienyl manganese tricarbonyl (MMT), which has been already approved for the use in several countries (Howe et al., 2004).

Potassium permanganate (KMnO₄) has long been used as an oxidizing catalyst in chemical processes, and in the disinfection in medicine, as well as in the purification of various waters. Also several other Mn compounds (e.g., gluconate, sulfate) are used in pharmaceutical production.

TABLE 12.2
Abundance of Mn (mg/kg) and Re (μg/kg) in Rocks and Soils

Rock/Soil	Mn	Re
Earth's crust	716–1400	0.4
Igneous rocks	—	—
Mafic	850–2000	0.4
Acid	350–1200	0.6
Sedimentary rocks	—	—
Argillaceous	400–850	0.5
Sandstones	100–500	0.1
Calcareous	200–1000	0.1
Soils ^a	488 ^b	0.4 ^b
Arenosols (sandy)	7–2000	
Podzols (medium loamy)	50–9200	
Cambisols (heavy loamy)	100–3900	
Calcisols (calcareous)	50–7750	
Histosols (organic)	10–2200	

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil average (Table 3.2).

B SOILS

Manganese contents of worldwide soils vary from 411 to 550 mg/kg (Table 3.2). Its highest levels occur in loamy and calcareous soils (Table 12.2).

During weathering, Mn compounds are oxidized under atmospheric conditions and released Mn oxides are reprecipitated and readily concentrated in forms of secondary Mn minerals. The behavior of Mn in surficial deposits is very complex and is governed by different environmental factors, of which Eh–pH conditions are the most important. Mn is easily removed, under cold climatic conditions, from the zone of weathering and from soils by acid solutions as bicarbonate or as complexes with SOM. Under tropical and subtropical conditions, however, Mn may be concentrated in various forms, often as concretions and nodules.

Manganese is relatively mobile in soil media. Its ionic species, commonly occurring in soil solutions, are as follows (Kabata-Pendias and Sadurski, 2004):

- Cationic forms: Mn^{2+} , MnOH^+ , MnCl^+ , MnHCO_3^+ , $\text{Mn}_2(\text{OH})_2^{2+}$, $\text{Mn}_2\text{OH}^{3+}$
- Anionic forms: MnO_4^- , HMnO_2^- , $\text{Mn}(\text{OH})_3^-$, $\text{Mn}(\text{OH})_4^{2-}$

The negatively charged $\text{Mn}(\text{OH})_4^-$ and MnO_2^- are responsible for the high degree of association of Mn concretions with some trace metals, in particular with Co, Ni, Cu, Zn, Pb, Ba, Tl, W, and Mo (Table 4.3). In addition, the oxidation of As, Cr, V, Se, Hg, and Pu by Mn oxides is likely to control the redox behavior of these elements in soils.⁹³³ The intensive studies on Mn behavior in soils have been carried out by a number of scientists, and their findings are reviewed in Chapter 4, Section III. McKenzie^{524,526} and Bartlett⁹³³ have summarized the present knowledge related to the soil Mn. They stated that Mn is likely to occur in soils as oxides and hydroxides in the form of coatings on other soil particles and as nodules of different diameters. The nodules often exhibit a concentric layering that is suggestive of seasonal growth.

Manganese may form a number of simple and complex ions and also several oxides in the soil solution (Figure 12.1). The Mn oxides in soils are mostly amorphous, but crystalline varieties have also been identified in several soils. As Norrish⁵⁷⁰ stated, lithiophorite, $(\text{Al}, \text{Li})\text{MnO}_2(\text{OH})_2$, is most

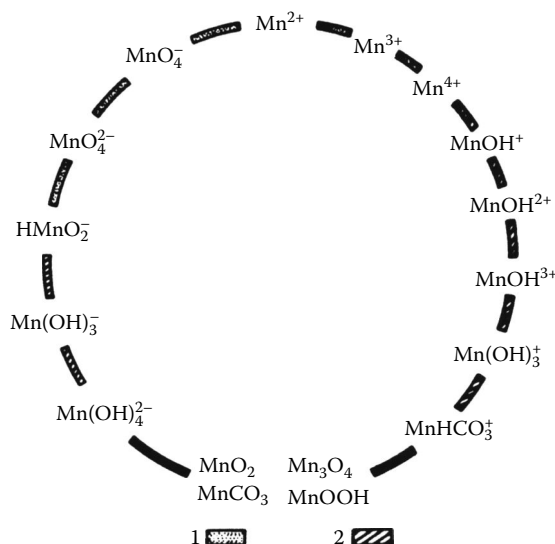


FIGURE 12.1 Ionic species and transformation of manganese compounds in soils. (1) Redox reactions; (2) redox and hydration reactions.

likely to occur in acid and neutral soils, while birnessite (unconfirmed composition, $\text{Na}_{0.7}\text{Ca}_{0.3}\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$) was reported to be in alkaline soils. However, a number of other crystalline forms of Mn oxides were observed in soil horizons. Of all the Mn oxides, the most stable under oxidizing conditions are pyrolusite, manganite, and hausmannite. Bartlett⁹³³ described the redox cycling of Mn in soils, and emphasized its role as scavenger for biodestructive free radicals at interfaces and as a redox transformation system. According to Negra et al. (2005), the $\text{Mn}^{4+}:\text{Mn}^{3+}$ ratio in soil control the oxidation state and pH values. The following sequence for Mn-redox cycling has been proposed:

- The reduction: $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$, abiotic and biotic, by Fe^{2+} , Cr^{3+} , S, phenols, organic compounds (humic substances), and reducing bacteria.
- The oxidation: $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$, Mn^{4+} , can occur under both aerobic and anaerobic conditions and is biologically mediated or autocatalytic.
- The Mn^{3+} is extremely reactive redox species and quickly disappears, either by accepting or by donating an electron.
- The Mn^{2+} is either adsorbed by MnO_2 , or oxidized to Mn^{3+} , or Mn^{4+} .
- The organic and phosphate ligands are also involved in Mn-redox cycling.

Presence of Mn in soil is the key to the entire status of soil redox (Sparks 1999). Data presented by Nelson and Lion (2003) indicated that biogenic, amorphous Mn oxides exhibit greater specific surface areas than typical abiotic Mn oxides. The adsorption capacity for metals increases with increasing pH (Wilson et al., 2001). In the case of Pb this increase is from about 20% to 80% of the total Pb concentration in solution, at 5 and 8 pH, respectively.

Megonigal et al. (2003) have emphasized that biologically mediated processes are the most significant in the Mn-redox cycling in soils. This statement has been supported recently by several other findings. Tani et al. (2003) reported that Mn oxides enzymatically produced by Mn-oxidizing fungus reveal specific adsorption properties to Co, Ni, Zn, and As. Glasauer and Beveridge (2003) described the dissimilatory reduction of Mn by bacteria attached to the surface of Mn-oxide minerals. Some organic acids secreted by microorganism can release Mn from synthetic MnO_2 (Jones, 1998).

Mn oxides have relatively high total surface (32–300 m^2/g) and CEC values (150–320 $\text{cmol}(+)/\text{kg}$). Metal species bound to Mn oxides in metal-polluted soils made up: <1–30% of total Cu; 1–26% of Pb; 3–27% of Zn; <1% of As; and <1% of Fe (Karczewska, 2004; Kabała and Wilk, 2004). The sorption of Co by Mn oxides, resulting in the Co valence changes and its unavailability to plants, has been of great importance in Australian sheep farming.⁹⁹⁷

The distribution of Mn among soil fractions was investigated using ^{54}Mn tracer (Goldberg and Smith, 1984). The results indicated that the distribution of Mn in soil fractions varies depending on soil groups (pedological origin). However, the fraction of resistant Mn minerals (oxides) contains usually the highest proportion of the metal, about 50% of the total contents. Mn is not distributed uniformly in soil substrata and, in addition to various nodules, is known to be also concentrated at certain spots which are usually enriched in several other trace elements. Colloidal Mn oxides reveal a great affinity for adsorption of cationic and anionic forms of elements as well as inorganic and organic substances. Thus, Mn oxides have a great impact on the immobilization of trace metals in soils. On the contrary, due to both reducing and oxidizing properties, Mn oxides can increase the mobilization of some metals under specific soil conditions.

All Mn compounds are very important soil constituents because this element is essential in plant nutrition and controls the behavior of several other micronutrients. It also has a considerable effect on some soil properties, and in particular on the poisoning system of Eh and pH. Mn compounds are known for their rapid oxidation and reduction under variable soil environments and thus oxidizing conditions may greatly reduce the availability of Mn and associated micronutrients, whereas reducing conditions may lead to the ready availability of these elements even up to the toxic range.

The reduction of Mn oxides has dual effects on soil cation exchange. Activity and susceptibility to leaching of Ca, Mn, and several other metals increases as Mn reduces. Bartlett⁹³³ also suggested a possible role of Mn oxides in nonmicrobial conversion of nitrite into nitrate, although no one has shown that such a reaction can occur in soils.

The mobility Mn in soils is highly dependent on the Eh–pH potential; therefore, the most common reactions that control Mn behavior in soils are oxidation–reduction and hydrolysis. Although the solution of Mn species as a function of Eh–pH conditions is demonstrated on the diagrams by Lindsay,⁴⁷⁷ the comparison of actual Mn levels in soil solutions with those predicted by the chemical equilibrium reactions has not met with success. The mixed and metastable composition of Mn oxides and hydroxides, organic complexes of Mn, and variable Eh–pH soil conditions are the main factors responsible for the lack of correspondence between actual and predicted Mn levels.

Because of a low solubility of Mn compounds in oxidizing systems at pH levels near neutrality, small shifts in the Eh–pH conditions can be very important in the Mn content of the soil solution. Concentrations of Mn in soil solutions vary highly from 25 to 2000 $\mu\text{g/l}$, depending on soil kinds and techniques used for obtaining solutions.¹³⁵⁷ The mobility of Mn is especially affected by soil pH. Concentrations of Mn in solutions of metal-polluted soils vary highly depending on soil pH. These changes are by a factor from 7.6 to 270 for acid soil (pH 2.5) and alkaline soil (pH 9–10), respectively (Karczewska, 2002).

Several soil factors influence the Mn availability to plants. The solubility of soil Mn is of significance since the plant supply of Mn depends mainly on the soluble Mn pool in the soil. In well-drained soils, the solubility of Mn always increases with the increase of soil acidity. However, the ability of Mn to form anionic complexes (Figure 12.1) and to complex with organic ligands may contribute to increased Mn solubility in the alkaline pH range (Figure 12.2). Among abiotic and biotic soil parameters, the complexing by root exudates and cross-interactions with Fe oxides play a crucial role. However, the ability of Mn to form anionic complexes and organic ligands may contribute to increased Mn solubility, even at the alkaline pH range. In general, Mn is highly mobile at the acid range of pH. In specific soil redox conditions, as for example, poorly aerated soil at pH about >6.0 or well-drained soils, at pH < 5.5, the Mn mobility increased, and Mn became easily available to plants.

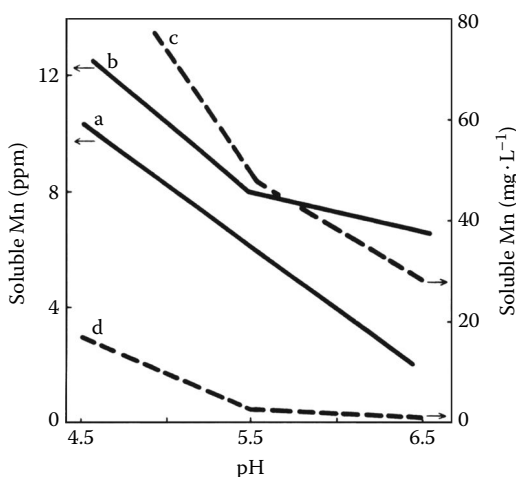


FIGURE 12.2 Solubility of soil Mn at different pH values. (a) In 0.01 M CaCl_2 from bulk soil; (b) in 0.01 M CaCl_2 from rhizosphere soil; (c) in 0.01 M citrate solution; and (d) in root exudates, after 72 h. (From Godo, G. H. and Reisenauer, H. M., *Soil Sci. Soc. Am. J.*, 44, 993, 1980. With permission.)

Hodgson et al.³²⁰ reported that the soluble Mn in soil solutions is mainly involved in organic complexing. In the surrounding soil of plant roots, the reduction of MnO_2 forms, and complexing by root exudates is apparently a significant factor controlling Mn mobility.²⁷⁰ Cheshire et al.¹³⁶ found that Mn in topsoil was largely associated with FA, but the Mn^{2+} bound to these compounds was highly ionized.

Microbiological soil activity is also known to be largely responsible for the oxidation and reduction of Mn compounds, as well as for the formation of Mn concretions, as described by several authors (Letunova et al.,⁴⁶⁶ Bromfield,¹⁰³ Wada et al.,⁸³⁶ and Aristovskaya and Zykina³⁶). Zajic⁸⁹⁸ and Weinberg⁸⁵⁶ reviewed several microbiological processes which directly or indirectly affect the transformation of Mn compounds in soils. The microbial dissolution of Mn compounds in soils, especially due to the enzymatic reduction of oxidized Mn (+3 and +4) and due to the production of CO_2 and organic acids, is of great importance. These processes are likely to occur at acid pH and appropriate Eh in soils. Where Fe accompanies Mn compounds in a solid phase, microbes may separate Mn from Fe by preferential solubilization. Some microorganisms, on the other hand, can precipitate Mn by oxidizing Mn^{2+} to Mn^{3+} and Mn^{4+} or stimulating the precipitation of carbonates, sulfides, etc.

The soil Mn has been the object of much research, and a great proportion of the studies has been related to the Mn phytoavailability. The availability of Mn to crop plants is of growing concern for some soils, and as Finck⁹⁹⁵ stated, an increase of the mobilization rate by soil acidification proves to be effective. Several extractants have been widely investigated for soil testing analysis. The best correlation with Mn uptake by plants was usually obtained for the water-soluble, the exchangeable, and the reducible fractions of soil Mn. According to Obrador et al. (2007), the highest proportion of Mn (13–51%, mean 30.9% of total content) is associated with the MnOX fraction, and its availability may be predicted, based on some empirical equations. Increased mobility of Mn with lower soil pH resulted in increased phytoavailability and losses of Mn from terrestrial catchments (Watmough et al., 2007). In soils that have to be heavily limed for structural reasons, the availability of Mn is limited. On the contrary, in soils with an increased mobility of Mn (e.g., well-drained soils at pH levels below 5.5, poorly aerated soils at pH of about 6.0 or higher), the variation of Mn content of surface soils rarely seems to be correlated with soil typology, but is positively associated with clay contents (Tables 12.2).

Higher Mn levels are often reported for soils over mafic rocks, for soils rich in Fe and/or organic matter, and for soils from arid or semiarid regions. Although Mn can be concentrated in various soil horizons, particularly in those enriched in Fe oxides or hydroxides, usually this element is also accumulated in topsoils as the result of its fixation by organic matter.

Mn budgets (input/output ratios) in soils of various ecosystems indicate a predominance of leaching processes over atmospheric input. In pine, spruce, and birch forests its leaching from soil profiles accounts from 360 to 6100 g/ha/year, whereas in other ecosystems some accumulation (91–191 g/ha/year) of Mn was observed (Table 3.13).

On the world scale, the range of Mn average contents of soil varies from 270 (in Podzols) to 525 mg/kg (in Cambisols). The grand mean calculated for world soils is 488 mg/kg, while for the U.S. soils the calculation is 495 mg/kg. The concentration of acid-soluble Mn in Finnish soils, at the 90th percentile, is 280 mg/kg, whereas total Mn (H_2F_2 fusion) is 600 mg/kg.¹³⁶⁸ Median contents of Mn in soils of Lithuania vary, depending on the kind of parent material, from 245 mg/kg in soils derived from eolian sediments to 605 mg/kg in soils on loamy clay glacial sediments.¹³⁵⁹ The highest Mn content, up to 9200 mg/kg is reported for soils derived from basalts and andesites in Australia.⁸⁶¹ Also in several other soils, mainly of Cambisols group, from various countries, the Mn concentrations reach up to 4000 mg/kg and average within the range of 800–1000 mg/kg. Relatively high Mn contents, up to 8510 mg/kg, are reported for some top soils of the Slovak Republic (Čurlik and Šefčík, 1999).

Manganese has not been considered to be a polluting metal in soils; however, the MAC value for this metal in agricultural soils is estimated at the range 1500–3000 mg/kg. The major anthropogenic

sources of Mn are: municipal wastewaters, sewage sludge, and metal smelting processes. The combustion of fuel additives (MMT) is of a lesser importance. However, in some regions (e.g., Mississippi River Delta) alluvial sediments can concentrate Mn up to >1000 mg/kg from MMT fuel use (Mielke et al., 2002). In contaminated riparian areas, soils contain Mn up to 2700 mg/kg (Shanahan et al., 2007). In soils irrigated with water affected by acid mine drainage the soluble Mn fraction increases due to reductive dissolution of Mn oxides (Green et al., 2003). Grove and Ellis²⁸⁹ found more water-soluble Mn in soil after fertilization with sludge. Hemkes et al.³¹⁴ reported the increase of Mn from 242 to 555 mg/kg in sludge-amended soil in 5 years. Diez and Rosopulo¹⁷⁶ observed a lower Mn uptake by plants from soil after sludge application. When Mn has accumulated in topsoil due to the Mn application over a long period of time, toxic effects in some plants might be observed.

C PLANTS

1 Absorption and Transport

Adequate levels of available Mn in growth media are necessary in plant nutrition. All findings give ample evidence that the Mn uptake is metabolically controlled. Skinner et al. (2005) reported that its transport across the soil–root interface is in the reduced, Mn^{2+} , state, apparently in a way similar to that of other divalent cation species such as Mg^{2+} and Ca^{2+} . However, passive absorption of Mn is also likely to occur, especially in the high and toxic range of its concentrations in the soil solution. Generally, Mn is known to be rapidly taken up and translocated within plants; therefore, it is likely that Mn is not binding to insoluble organic ligands, either in root tissue or in xylem fluid.

Complex interactions between roots and microorganisms may affect the phytoavailability of Mn (Marschner and Rengel, 2005). Deficiency of Mn is relatively common in certain crops grown in neutral and calcareous soils. In such soils, the interactions of plant roots with microorganisms (in the rhizosphere) can facilitate the oxidation of soluble Mn^{2+} into unavailable Mn^{3+} or Mn^{4+} (Rengel, 2004).

Manganese is reported to occur in plant fluids and extracts mainly as free cationic forms.^{789,798} It appears, therefore, that Mn is likely to be transported as Mn^{2+} , but its complexing compounds with organic molecules also were found in phloem exudates.⁸²² Van Goor^{820a} reported a much lower Mn concentration in phloem exudate than in leaf tissues and concluded that a slight transport of Mn through the phloem vessels is responsible for low concentrations of Mn in fruits, seeds, and storage roots. Mn is preferentially transported to meristematic tissues, thus its concentration is mostly observed in young expanding tissue. Heenan and Campbell³⁰⁹ reported that at a high Mn supply, the leaves accumulated higher concentrations with age, but small amounts of Mn were translocated from old leaves when young expanding leaves were Mn deficient. Thus, Mn appeared to have a low mobility when the supply to a plant is limited. Mn concentrations fluctuate greatly within the plant parts and within the vegetative period. Scheffer et al.^{688a} reported a relatively low Mn level in barley during intensive growth and further Mn accumulation in old leaves and sheaths.

It should be emphasized, however, that the Mn content of plants is not only an effect of plant characteristics, but also of the pool of available Mn, which is highly controlled by soil properties. Generally, the most readily available Mn is in acid and flooded soil. More than a tenfold increase in the Mn content of lucerne (alfalfa) was observed in plants grown on flooded soil, compared to background values.⁵³¹ Therefore, the reducing ability of root exudates and of bacteria in the rhizosphere apparently is of direct importance in the Mn nutrition of plants.²⁷⁰

Because Mn seems to be easily taken up by plants when it occurs in mobile forms in soils, and Mn content of plants is a direct function of the soluble Mn pool in soils. And indeed, Mn concentration in plants shows a negative relationship with increasing soil pH and a positive relationship with soil OM (Figure 12.3).

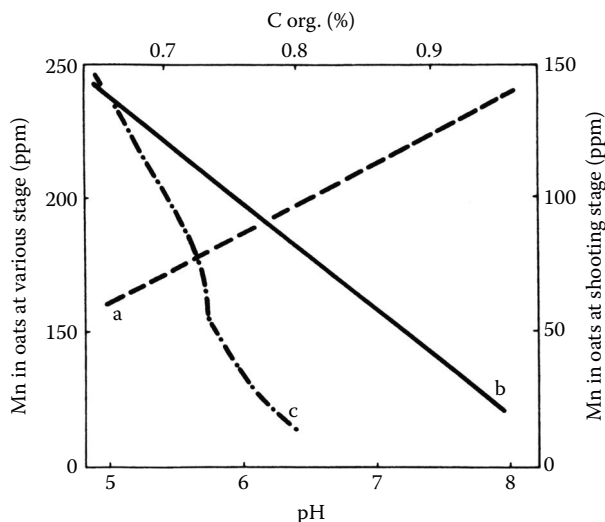


FIGURE 12.3 Influence of soil factors on the Mn content of oats. (a) Organic matter added as slurry, oats at various stages of growth; (b) pH adjusted with H_2SO_4 or CaO , oats at various stages of growth; (c) pH resulting from fertilization with different N-fertilizers, oats at shoot stage. (Data compiled from Kukurenda, H. and Lipski, R., *Pamiet. Pulawski*, 76, 172, 1982 (Po); Schung, E. and Finck, A., Paper presented at 9th Int. Coll. Plant Nutrition, Coventry, August 22, 1982, 582.)

An excess of phytoavailable Mn is associated with several soil properties, such as:

- Strongly acid soils (pH levels of 5.5 or below)
- Anaerobic condition and poor aeration (flooded, waterlogged, or compact soils)
- Heavily limed soils (raised pH levels up to about 8)

2 Biochemical Functions

All plants have a specific requirement for Mn and apparently the most important Mn function is related to the oxidation–reduction processes. The functions of Mn in plants have been widely reviewed by Shkolnik,⁷¹⁸ Boardman,⁸³ and Mengel and Kirkby.⁵³¹ Mn^{2+} is known to be a specific component of two enzymes, arginase and phosphotransferase, but this metal can also substitute for Mg in other enzymes. The mechanism by which Mn^{2+} activates several oxidases is not yet known precisely, but it appears to be related to the valency change between Mn^{3+} and Mn^{2+} .

Manganese appears to participate in the O_2 -evolving system of photosynthesis and also plays a basic role in the photosynthetic electron transport system. Apparently, the Mn fraction that is loosely bound in chloroplasts is associated with O_2 evolution, whereas the firmly bound Mn fraction is involved in the electron pathway in photosynthesis. Bartlett⁹⁹³ described Mn as a key to life and emphasized its role in O_2 evolution in the photosynthesis. The role of Mn in the NO_2^- reduction step is not yet clear, but it appears to be a kind of indirect relationship between the Mn activity and N assimilation by plants.

Chloroplasts are the most sensitive of all cell components to Mn deficiency and react by showing structural impairment. Deficiency symptoms occur first in younger leaves as interveinal chlorosis. At further stages, necrotic, reddish and brownish spots on leaves, and browning of roots appear. The growth of Mn-deficient plants is retarded, the turgor is reduced, and plant resistance to diseases and frost is lower (Table 5.10). Plants deficient in Mn apparently are less frost hardy.^{383,511} The most sensitive to the Mn deficiency are oats (gray speck symptoms), peas (marsh spot symptoms), sugar beet, and some fruit trees. The optimum rates and the methods of Mn applications, as soil fertilizers and foliar application, have been extensively reviewed in several textbooks. However, a high rate of

Mn application or use of inappropriate forms, as well as variable soil conditions, can easily result in toxic effects on plants.

Although Mn deficiency is relatively common in certain crops grown on neutral and calcareous soils, diagnosis and correction of the deficiency is not well-defined. Since soil analysis is not very reliable in diagnosing the Mn supply to plants, tissue tests should be considered together with soil and field observations. The correction of Mn deficiency in crops may be done by both soil and foliar application. The optimum rates and the method of Mn application is extensively reviewed in several textbooks.^{556,649,847} Most crop plants do not suffer from Mn deficiency at concentrations above the range of 15–25 mg/kg. Rengel (2004) reported that Mn concentrations in the phloem sap range from 2 to 910 $\mu\text{M/L}$, whereas the required concentration, to keep the minimal levels of Mn in grains (10–20 mg/kg), ranges between 25 and 100 $\mu\text{M/L}$.

Toxicity of Mn to some field crops might be expected on acid soils of pH around 5.5 or lower and with a high Mn level. However, the critical Mn content and unfavorable soil pH ranges depend upon several other environmental factors. Mn toxicity is also known to occur at higher pH levels in poorly drained (poorly aerated) soils. However, if acid soils are very low in total Mn, plants are not subjected to Mn toxicity. As Beckwith et al.⁶⁰ reported, flooding did not always increase Mn uptake by rice shoots, since flooding may also increase soil pH and therefore decrease Mn uptake. As reviewed by Andersson,⁹²¹ there are great differences between species in the sensitivity to Mn. For example, most sensitive false oat grass showed a significant decrease in biomass at the Mn concentration of 5 mg/L, while marsh bent grass was unaffected even by 200 mg/L in the solution. Foy et al.^{998a} discussed correcting or preventing Mn toxicity by conventional liming or soil drainage practices and emphasized that the most reasonable approach to the problem is to select or breed plant genotypes having greater tolerance to excess Mn in soils. Most often, plants growing on acid soils tolerate high Mn concentrations. Foy⁹⁹⁸ described that Mn tolerance is related to several characteristics and metabolic processes, such as:

- Oxidizing power of plant roots, possible oxidation of Mn to MnO_2 , which is stored as inactive fraction
- Mn absorption and translocation rates
- Complexation of Mn by low-molecular-weight compounds produced by plant roots or soil microorganisms
- Mn entrapment in nonmetabolic centers
- Interactions with other elements, especially with Ca, Fe, Al, Si, and NH_4

Steam sterilization of greenhouse soils is known to increase the available Mn to levels toxic to certain plants. This phenomenon is closely linked with soil biological activity (Chapter 4, Section IV). Foy et al.^{998a} reviewed Mn–microbial relationships and emphasized remedial effects of various microorganisms (especially *Rhizobia* and *Mycorrhiza* strains) on resistance of plants to Mn toxicity. The Mn toxicity in plants is complex and interrelated with other elements. Foy⁹⁹⁸ reported impaired effects of high levels of Mn on the activity of some enzymes and hormones (e.g., auxin, gibberellin) and also on the proportion of amino acids. The response of plants to excessive Mn levels is highly controlled by differences between genotypes. Brown and Devine¹⁰⁵ stated that the control of tolerance to excess Mn appeared to be multigenic and was apparently related to Fe metabolism in plants. Legumes appear to be more sensitive, because Mn excess affects rhizobia nodule numbers and thus the efficiency of the N fixation. The results of studies carried out by Watanabe et al.¹⁵³⁹ show that the Mn in leaf tissues occurs as a mixture of soluble salt $\text{Mn}(\text{OH})_6^{2+}$ and organic components containing Mn-porphyrins, but is translocated in xylem mainly as free divalent cation. Leaves with bronzing symptoms contain large amounts of Mn; for example, in injured bean leaves, the Mn level was $>760 \text{ mg/kg}$.¹³⁰⁹

The most common symptoms of Mn toxicity are Fe chlorosis and brown spots on leaves. Leaf puckering, necrotic brown spots, and an uneven distribution of chlorophyll in older leaves are also symptoms of Mn toxicity. In severely injured plants, browning of roots occurs (Table 5.12). Also, an

increased Fe uptake by these plants has been observed.^{114,340} Symptoms of Mn toxicity are more pronounced in warm and hot weather.

There is a great difference between plant species and genotypes in the sensitivity to Mn. Among crop plants, cereals, legumes, and potatoes are the most sensitive to the Mn excess in growth media. The physiology of Mn toxicity is associated mainly with impaired impact on the activities of some enzymes and hormones, as well as on amino acid synthesis. Plants resistant to Mn excess have an ability to accumulate Mn in roots and/or to precipitate MnO_2 within the epidermis. Generally, most plants are affected by Mn contents around 500 mg/kg. However, the accumulations above 1000 mg/kg in some resistant plant species or genotypes, and up to 10,000 mg/kg in hyperaccumulators have been reported (Greger, 1999).

3 Interactions with Other Elements

Manganese is known to be involved in both biological and geochemical interactions (Figure 5.8). The most prominent geochemical interference is observed in the strong affinity of Mn oxides for Co. This reaction is so marked that most of the native Co in soils may be unavailable to plants in the presence of moderate amounts of Mn.^{524,526} The strong absorption capacity of Mn oxides for other trace metals may also highly govern the availability of these metals to plants.

Mn–Fe antagonism is widely known and is observed mainly in acidic soils that contain large amounts of available Mn. In general, Fe and Mn are interrelated in their metabolic functions, and their appropriate level (the Fe:Mn ratio should range from 1.5 to 2.5) is necessary for the healthy plant. Below this range, symptoms of Mn toxicity and Fe deficiency may occur; and above 2.5, toxic effects of Fe, associated with the Mn deficiency, will be observed. Alvarez-Tinaut et al.¹⁶ reported that both deficient and normal Mn levels antagonize the Fe absorption, but the reverse influence was true when Mn reached toxic concentration in plants. In certain field and crop conditions, both Mn or Fe toxicity can be remedied by Fe or Mn application.²⁴¹ Peng et al. (2008) observed that Mn added to the nutrient solution reduced the Cd concentrations in all organs of a plant (*Phytocacca Americana* L.).

Interactions between Mn and other trace metals are not confirmed, although there are reports of either antagonistic or synergistic effects of Mn on the uptake of Cd and Pb,³⁸¹ and Zn depressing effects on the Mn uptake.¹⁰⁷⁴ The interactions of Mn and P may be cross-linked with Fe–P antagonism or related to both the variation in the Mn-phosphate solubility in soils and the Mn influence on P metabolic reactions. Depending on soil conditions, P fertilizers are known to either aggravate Mn deficiency in oats or to increase Mn uptake by other plants. These phenomena are closely related to the soil pH and soil sorption capacity.

Interactions of Mn and Si have been reported by several authors. An adequate Si supply to plants is reflected in the easy transport of Mn and a more homogeneous Mn distribution in the plant.³²⁶ Plants deficient in Si are known to accumulate more Mn than Si-sufficient plants. There are several indications that an available Si supply reduces the Mn toxicity to plants.²⁴¹ Antagonistic effects of Ca and Mg on Mn uptake seem to have a complex character. Foy⁹⁹⁸ found that the excess of Mn induces Ca deficiency because it inhibits the transport of Ca within plants, and Ca, under certain conditions, reduces the Mn toxicity.¹⁰⁹⁸ Antagonistic interactions are also observed between Mn and K, Na, and N (Table 5.11). Although there are evidences of both antagonistic and synergistic interactions, apparently more data are required in this field. Several interactions between Mn and other trace elements have been observed, but are not fully confirmed, and in most cases might be cross-linked with macro-elements. For example, P and Ca may affect either a Mn deficiency or elevated Mn uptake, depending on plant characteristic and/or soil properties.

4 Concentrations in Plants

Manganese shows a particularly wide variation among plant species grown on the same soil, ranging from an average of 30 mg/kg in *Medicago trunculata* to around 500 mg/kg in *Lupinus albus*.⁴⁸⁹ Similarly, a wide range of Mn has been observed in forage plants as reported for different countries.

TABLE 12.3
Mean Levels and Ranges of Mn Grass and Clover at the Immature Growth Stage from Different Countries (mg/kg)

Country	Grasses		Clovers		Ref.
	Range	Mean	Range	Mean	
Australia	67–187	120	33–43	38	266
Great Britain	79–160 ^a	—	31–65 ^a	—	67
Czech Republic	24–130	71	17–42	25	154, 562
Finland	41–144	77 ^b	33–205	119	388, 727
Germany	35–106	70	24–420	71	576, 596
Hungary	67–309	161	55–126	82	803
Ireland	77–116	86	18–39	26	235
Japan	20–330	127	15–436	89	770
New Zealand	49–139	114	29–165	77	536
Poland	20–665	98	16–260	58	1045
U.S.	80–1840	334 ^c	—	—	15
Russia	26–493	44	19–165	70	338
Yugoslavia	16–18	17	—	—	755

^a From freely and poorly drained soils, respectively.

^b Timothy grass.

^c Samples from grass tetany pasture.

Worldwide contents of Mn range from 17 to 334 mg/kg in grass and from 25 to 119 mg/kg in clover (Table 12.3).

Plant foodstuffs are also reported to contain variable amounts of Mn, being the highest in beet roots (36–113 mg/kg) and the lowest in apples (1.3–1.5 mg/kg). The Mn content shows a remarkable variation for plant species, stage of growth, and different organs as well as for different ecosystems. A relatively small variation has been observed in the Mn content of cereal grains, which average from 18 to 48 mg/kg throughout the world (Table 12.4).

The critical Mn deficiency levels for most plants ranges from 15 to 25 mg/kg, whereas the toxic concentration of Mn to plants is more variable, depending on both plant and soil factors. Generally, most plants are affected by a Mn content at above 400 mg/kg (Table 5.8). However, the accumulation above 1000 mg/kg also has been often reported for several more resistant species or genotypes (Shanahan et al., 2007, Min et al., 2007, Ferrando, 2010, Ivlev et al.³⁴⁵). The hyperaccumulator plants (*Phytoacca Americana* L.) absorbed Mn from the contaminated soil up to 13,400 mg/kg in leaves (Peng et al., 2008).

II TECHNETIUM

A INTRODUCTION

Technetium is a by-product of nuclear fuel processing, and the only artificial metal that is used in metal processing. Metallic Tc, mainly used in alloys with Mo or Nb exhibits electrical superconductivity and is very resistant to the oxidation, it may be added to some Fe-alloys, to inhibit the corrosion. Minute quantities of the most common isotope ⁹⁹Tc are found in uranium ores (Fairbridge, 1972). It also may be captured in Mo ores.

This isotope is widely used in medicine for the diagnostic of thyroid disorders and other medical x-ray diagnostics.

TABLE 12.4
Range and Mean Mn contents of Food Plants^a (mg/kg)

Plant	Range	Mean
Wheat, grains	16–103	40
Wheat, grains ^b	24–29	27
Wheat, grains ^c	8–53	25
Wheat, grains ^d	37–88	48
Barley, grains ^c	12–34	18
Rye, grains	10–87	30
Oats, grains	17–121	50
Pea, yellow, seeds	—	21
Bean, pods ^b	4–25	21
Carrot, roots	9–28	15
Carrot, roots ^b (FW)	1–1.9	1.3
Onion, bulbs	16–24	19
Beet (sugar and red), roots	36–113	80
Potato, tubers	4–15	9
Potato, tubers ^b (FW)	0.4–0.9	1.2
Tomato, fruits	—	12
Apple, fruits	1.3–1.5	—
Strawberry, fruits ^b (FW)	1–1.9	1.3
Nuts and almonds ^c	10–42	22

^a Possible background worldwide values from various sources.

^b After Szteke B., Jędrzejczak R., Ręczajska W. 2004. *Ann. Nat. Inst. Hygiene*, Suppl. 55:21–27 (in Polish); samples from Poland.

^c After Eriksson J.E. 2001. Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertilizers, precipitation and in oil and crops. Swedish EPA. Rep 5159. Stockholm; samples from Sweden.

^d After Škrbić B., Onjia A. 2007. *Food Control* 18:338–345; samples from Serbia.

^e After Jędrzejczak R. 2004. *Ann. Nat. Inst. Hygiene*, Suppl. 55:13–20 (in Polish); samples from markets in Poland.

B SOILS AND PLANTS

Geochemical properties of Tc are similar to those of Mn and Re, however it is very easily fixed by soil particles. In compounds, Tc occurs mainly as heptavalent (+7 oxidation), and forms the pertechnetate anion TcO_4^- . Adsorption of pertechnetate ion on mineral surface is weak and tends to be strongly affected mainly by pH, while reduced Tc is readily sorbed by soils constituents and also forms complexes with OM (Zhang et al., 2002).

The source of ^{99}Tc is mainly global fallout from nuclear fissions. According to Tagami and Uchida^{1512a} contents of this radionuclide in paddy soils of Japan vary from 6.1 to 110 mBq/kg, being accumulated in surface soil layers. The soil to rice-plant transfer of Tc is much lower in flooded soil than in nonflooded soil. Apparently it is controlled by the ratio of two Tc species, soluble TcO_4^- , and insoluble TcO_2 (Yanagisava and Muramatsu¹⁵⁶⁰).

The transfer factor of Tc from soil to vegetables ranges and is the lowest for tomato (BCF—0.3) and the highest for spinach (BCF—17).¹⁵⁶⁰ Recent studies have indicated that the Tc bioavailability in natural soils environments is lower than expected (Tagami and Uchida, 2005). The phytoavailability of reduced Tc is much less than that of pertechnetate (Zhang et al., 2002). In plants, Tc is relatively immobile, therefore the highest Tc concentrations were found in older plant tissues.

Denys et al. (2005) reported that the correlation between TcO_4^- and NO_3^- might be useful to assess the fate of ^{99}Tc in soils. Organic and nitrogen fertilizers inhibit its phytoavailability since they stimulate changes of the mobile TcO_4^- to slightly soluble TcO_2 and TcS_2 (Echevarria et al., 1997). Tagami and Uchida (2005) proposed to use a rate of ^{183}Re uptake by plants as tracer for $^{99\text{m}}\text{Tc}$ abundance in soil, since the phytoavailability of both radionuclides are fairly similar.

The disposal of Tc-enriched wastes is an environmental hazard since it is easily included in the biocycle. It is subjected to microbial oxidation and reduction processes and is easily taken up by plants, possible as the anion TcO_4^- (Echevarria et al.¹²⁸⁷). However, in reduced groundwaters this radionuclide is likely to occur in the slightly mobile species, $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ (Hu et al., 2005).

III RHENIUM

A INTRODUCTION

Rhenium is highly dispersed in the Earth's crust and its concentrations in soils are fairly similar to that of rocks and averages from 0.4 to 0.6 $\mu\text{g}/\text{kg}$ (Tables 3.2 and 12.2). It occurs primarily in minerals of other elements and is commonly associated with molybdenite, zircon, and gadolinite. The mineral dzhezkazganite, CuReS_4 , containing 40–50% of Re, occurs rather seldom. Higher amounts of Re are also observed in some minerals of the LAs.

The most common oxidation state is +7, but other oxidation states are also known (Table 12.1). Two ionic forms Re^{4+} and Re^{6+} reveal similarity to Mo cations and are likely to substitute for this metal in geochemical processes. Thus, molybdenite can contain Re up to around 2%.

The annual global production of Re in 2008 was 57 tons (USDI, 2009). The use of Re is mainly in productions of lamps, photographic flashes, and thermostats. It is also used as catalyst in some chemical reactions. This metal is added to alloys used for medical tools and in jewelry production. The supplementation of Re compounds has been recently used in some cancer patient treatments.

B SOILS AND PLANTS

During weathering, Re is readily soluble, especially in oxidizing and acidic conditions, mainly as the anionic form, ReO_4^- . It is precipitated or sorbed by various sediments, such as bituminous copper shales, black piritic shales, as well as some coals, up to 10 mg/kg . Swedish arable soils contain Re at average value of $<40 \mu\text{g}/\text{kg}$ (Eriksson, 2001). Increased Re contents, up to 9.8 $\mu\text{g}/\text{kg}$, has been observed in soils along major motorways in Austria (Fritsche and Meisel, 2004).

Soluble forms of Re are apparently relatively easily available to plants. There are some evidences that Re is likely to be phytoextracted from soils and waters. Some plants from the ore-Re mineralization region accumulate extremely high amounts of Re that might be use for biotechnological production of this metal. Concentration of Re in leaves of plants from that region is (in mg/kg , AW) as follows: (1) acacia, 3.6–9.45; (2) birch, 0.98–4.1; and (3) *Arctostaphylo*, 30.8 (Buzhkov et al., 2008). Shacklette et al.⁷¹⁰ reviewed data on Re occurrence in plants and gave the range in Re concentrations in native vegetation of the United States as 70 to 300 mg/kg (AW). Barley and wheat grains from Sweden contained Re at the average value of $<0.1 \mu\text{g}/\text{kg}$ (Eriksson, 2001).

13 Elements of Group 8 (Previously Part of Group VIII)

According to the previous nomenclature system of the Periodic Table, the elements of the three groups 8, 9, and 10, were included in one Group VIII. The old system referred to chemical and geochemical properties of the elements and therefore it was easier to compare and describe these elements. However, the new nomenclature system is now obligatory. The Group 8 of the New Periodic Table of Elements (after the latest IUPAC recommendation) is composed of three elements: iron (Fe), ruthenium (Ru), and osmium (Os). These elements exhibit highly variable states of oxidation, as well as various properties ([Table 13.1](#)).

I IRON

A INTRODUCTION

Iron is the most important metal and one of the major constituents of the lithosphere. Its average content of the Earth's crust is about 5%. The global terrestrial abundance of Fe is calculated to be around 4.5% and it is not considered a trace element in rocks and soils. However, Fe plays a special role in the behavior of several trace elements and is in the intermediate position between macro- and micronutrients in plants, animals, and humans.

The geochemistry of Fe is very complex in the terrestrial environment and is largely determined by the easy change of its state of oxidation in response to physicochemical conditions. Fe is very reactive chemically and is similar in behavior to other metals, especially to Co and Ni. Its behavior is also closely linked to the cycling of O, S, and C. In variable environmental conditions, Fe reveals various characteristics and can be siderophilic, chalcophilic, or lithophilic. In most minerals formed near the Earth's crust surface, Fe occurs as the ferric (Fe^{3+}) ion, whereas in deeper rocks the ferrous (Fe^{2+}) ion predominates. However, it is known to occur also at +4 and +6 oxidation states in various complexes and in specific environments.

There are two recognized cycles of Fe: *exogenic* that takes place at the surface of the Earth's crust, and involves the action of water and air, and *endogenic*—taking place beneath the surface of the Earth, and includes geological processes, such as for example, melting, metamorphism.

The Fe ore minerals are mainly ferric oxides (e.g., hematite) or hydrated ferric oxide (goethite), and various dimorphous minerals, including those that are commonly occurring in soils. Important Fe ore deposits can also be composed of other Fe minerals, like siderite, FeCO_3 ; pyrite, FeS_2 ; and ilmenite, $\text{FeO} \cdot \text{TiO}_2$. “Bog ores” are small deposits of FeCO_3 resulted from the precipitation of soluble $\text{Fe}(\text{HCO}_3)_2$ in lakes, swamps, and shallow shelf regions.

The fate of Fe in processes of weathering is dependent largely on the Eh–pH system and on the stage of oxidation of the Fe compounds involved. The general rules governing the behavior of Fe are that oxidation and alkaline conditions promote the precipitation of Fe, whereas reducing and acid conditions promote the mobilization of Fe compounds. The complex geochemical behavior of Fe associated with its participation in oxidation–reduction processes, resulted, similarly as in the case of Mn, in the formation of great number of oxides and hydroxides. Several minerals and amorphous compounds of Fe have a large surface area that is involved in the reactions of various cations and anions in terrestrial environments. Iron complexes with organic ligands have a significant impact on

TABLE 13.1
Selected Properties of Trace Elements of Group 8

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C) (g/cm ³)	Valence ^b
Fe, iron	26	55.8	172	7.87	+2, + 3 , +4, +6
Ru, ruthenium	44	101.1	189	12.41	+ 3 , +4 ^c
Os, osmium	76	190.2	192	22.61	+ 3 , +4, +6, +8 ^d

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation states.

^c Oxidation states range between 0 and +8.

^d Oxidation states range between −1 and +8.

the metal's fate in the environment. A variety of humic and nonhumic organic compounds are involved in the Fe mobility in various terrestrial environments.

Microbial oxidation of Fe that can occur under both aerobic and anaerobic conditions stimulates the precipitation of poorly crystalline Fe oxides, which have significant impact on the behavior of several other cations (Megonigal et al., 2003). Microorganisms play a key role in Fe cycling, which is closely associated with organic carbon oxidation via Fe³⁺ reduction and with the transformation of sulfide and sulfate compounds. About 18 Fe minerals, oxides, hydroxides, carbonates, phosphates, sulfates, and sulfites are listed as possibly biologically induced (Frankel and Bazylinski, 2003). Siderophores are Fe-chelated compounds secreted by microorganisms (and possibly by grasses). Chelating ligands of siderophores are catecholates, hydroxamates, carbonates, and they are considered the greatest binders to Fe³⁺ with a significant role in Fe transport across cell membrane.

Since about 3000 years BC, Fe has been used by man and has played a dominant role in human civilization. It is the most commonly used metal in all civilizations. The calculation for 2008 gave the annual Fe production as raw steel at 1300 Mt, and as “pig iron” at 958 Mt (USDI, 2009). More than 90% of “pig iron” obtained from smelting furnace is processed further for the production of steel and various alloys. As a very chemically reactive metal, Fe tarnishes rapidly in air or water. Effects of corrosion processes, on a global scale, are a serious source of this metal in different environmental compartments.

B SOILS

The abundance of Fe in soils average 3.5% and is likely to be increased in heavy loamy soils and some organic soils (Table 13.2). The color of soils is largely associated with amounts and forms of Fe compounds. Therefore, a content and profile distribution of Fe compounds has been used for the description of soil processes and for the soil classification. As Zonn¹¹⁹⁶ emphasized, the speciation and distribution of Fe compounds in soils is very useful for the typology and diagnosis of soil properties.

The geochemistry of Fe is very complex in the terrestrial environment and is largely determined by the easy change of its valence states in response to the physicochemical conditions. The behavior of Fe is closely linked to the cycling of O, S, and C. The reactions of Fe in processes of weathering are dependent largely on the Eh–pH system of the environment and on the stage of oxidation of the Fe compounds involved. The general rules governing the mobilization and fixation of Fe are that oxidizing and alkaline conditions promote the precipitation of Fe, whereas acid and reducing conditions promote the solution of Fe compounds. The released Fe readily precipitates as oxides and hydroxides, but it also substitutes for Mg and Al in other minerals and often complexes with organic ligands.

In soils, Fe is believed to occur mainly in the forms of oxides and hydroxides as small particles or associate, in amorphous form, with the surfaces of other minerals. However, in soil horizons rich

TABLE 13.2
Abundance of Fe in Rocks and Soils (%%)

Rock/Soil	Fe
Earth's crust	4.5–5
Igneous rocks	—
Mafic	3.7–8.7
Acid	1.4–2.7
Sedimentary rocks	—
Argillaceous	3.3–4.7
Sandstones	1.0–3.0
Calcareous	0.4–1.0
Soils ^a	3.5
Arenosols (sandy)	0.1–1.0
Podzols (medium loamy)	0.8–2.8
Cambisols (heavy loamy)	1.5–3.0
Calcisols (calcareous)	0.1–0.5
Histosols (organic)	0.03–5.0

^a Soil groups are given according to the WBR (Table 3.1).

in OM, Fe appears to be mainly in chelated forms. Certain fractions of Fe in soils reveal magnetic properties. The increased ratio of magnetic Fe to regular Fe in a soil, as compared to mother rock, indicates the impact of industrial pollution.

Free Fe minerals that occur in soil are used as a key characterization for soils and for soil horizons. Fe minerals that are known to be also formed pedogenically are:

- Hematite, $\alpha\text{-Fe}_2\text{O}_3$, occurs mainly in soils of arid, semiarid, and tropical regions and is most often inherited from parent materials.
- Maghemite, $\gamma\text{-Fe}_2\text{O}_3$, is formed in highly weathered soils of tropical zones and most often occurs in concretions accompanied by hematite, magnetite, or goethite.
- Magnetite, Fe_3O_4 , is mostly inherited from parent materials; in soils, it is strongly associated with maghemite.
- Ferrihydrite, $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, is apparently a common, but unstable soil mineral and is easily transformed to hematite in warm regions and to goethite in humid temperate zones.
- Goethite, $\alpha\text{-FeOOH}$, is the most common Fe mineral in soils over broad climatic regions, from temperate to tropical. The crystallinity and composition of goethites vary and may reflect the environment in which they have formed.
- Lepidocrocite, $\gamma\text{-FeOOH}$, is common in poorly drained soils (e.g., paddy soils) and in soils of humid temperate regions. The formation of this mineral in soils is favored by lower pH, lower temperature, and the absence of Fe^{3+} .
- Ilmenite, FeTiO_3 , does not occur commonly in soils. As a mineral resistant to weathering, it is usually inherited from igneous parent rocks.
- Pyrite, FeS_2 ; ferrous sulfide, FeS ; and jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, are widely distributed in submerged soils containing S (e.g., acid sulfate soils).
- Vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$; and hydrous ferric phosphate, $\text{FePO}_4 \cdot n\text{H}_2\text{O}$ are formed mainly under the influence of bacterial processes.
- Schwertmannite, an iron-oxyhydroxysulfate mineral with very complex chemical formula, is formed in acid-sulfate soils associated with coastal lowlands.

Detailed descriptions of the role and behavior of Fe in soils have been presented by Bloomfield,⁸¹ Krauskopf,⁴²⁷ Lindsay,⁴⁷⁷ Norrish,⁵⁷⁰ and Schwertmann and Taylor.⁶⁹⁹ Both mineral and organic compounds of Fe are easily transformed in soils, and OM appears to have a significant influence on the formation of Fe oxides. These oxides may be amorphous, semicrystalline, or crystalline, even under the same conditions. Microorganisms appear to have a significant influence on the formation of Fe oxides, as well as on their forms (crystalline, semicrystalline, amorphous). Especially some bacteria (e.g., *Thiobacillum*, *Metallogenium* sps.) are involved in the accumulation and cycling of Fe (Megonigal et al., 2003). Various binding mechanisms between living organisms, like bacteria and fungus, and soil clay and OM play a crucial role in Fe forms and distribution. The precipitation of Fe due to the accumulation of $\text{Fe}(\text{OH})_3$ at a bacteria cell surface is relatively common process in soils (Paul and Clark, 2000).

Goethite is apparently the most frequently occurring Fe-mineral in soils and involved in sorption processes such as: (1) absorption of metals on external surface, (2) solid state diffusion of metals, and (3) metal binding and fixation at position inside the mineral particles. A strong ability of goethite to bind selected metals might suggest that this mineral as well as other Fe hydroxides could be used to ameliorate metal-polluted soils. Different authors have presented several orders of preferential sorption of metals by goethite. Most commonly, however, metal ion affinity for the Fe-oxide surface has been presented as follows: $\text{Cu} > \text{Zn}, \text{Co}, \text{Pb} > \text{Mn} > \text{Cd}$. Pett-Ridge et al. (2007) reported that amorphous Fe-oxides is the dominant control on U in soils due to great sorption capacity. According to Cheney et al. (2004) the adsorption of selenite and iodate onto goethite affects a low phytoavailability of Se and I in certain soils. In general, all Fe compounds and concretions in soils reveal a great sorption capacity to several trace elements and to metals, in particular (Table 4.3).

Results presented by Karczewska (2004) indicated that amounts of metals bound to both amorphous Fe oxides and crystalline iron oxides in metal-polluted soils are fairly similar and governed mainly by soil properties. Relative amounts of total metal contents bound to Fe oxides (in % of total contents) are as follows:

- By amorphous Fe oxides: Cu, 3–24; Pb, 1–54; Zn, 3–25; and As, 43–90.
- By crystalline Fe oxides: Cu, 5–29; Pb, 3–53; Zn, 15–34; and As, 5–46.

The distribution of Fe minerals and compounds in soil profiles is highly variable and reflects several soil processes. Many reactions are involved in the solubility of Fe in soil, but hydrolysis and formation of complexed species appear to be the most important. The solubility of Fe^{3+} and Fe^{2+} amorphous hydrous oxides especially control the mobility of soil Fe. Formation of other Fe compounds, such as phosphates, sulfides, and carbonates also greatly modify the solubility of Fe.

Soils developed on coastal sediments or on acid sulfate soils have very poor agricultural productivity because of their acidity. This acidity is a result of the oxidation of pyrite. At high pH, pyrite is oxidized chemically, but at pH values below 4.5, it is mediated by microorganisms. These processes may bring up a very low pH of soil and greatly influence the release of metals.¹¹³⁷

Several reactions are involved in the solubility of Fe in soil, but hydrolysis and complexed species appear to be most significant. Lindsay⁴⁷⁷ reported that the mobility of Fe in soils is largely controlled by the solubility of Fe^{3+} and Fe^{2+} amorphous hydrous oxides (Figure 13.1).

Contents of easily soluble and exchangeable fractions of Fe are very low in comparison with the total Fe content. Easily soluble species of Fe, determined as an operational group by sequential extraction, account from 0.01% to 0.1% of the total Fe, and exchangeable species account from 0.05% to 0.21% (Kabała and Wilk, 2004). The concentration of Fe in soil solution, at the common soil pH, ranges from 30 to 550 $\mu\text{g/L}$, but in very acid soils it can exceed 2000 $\mu\text{g/L}$. Thus, in calcareous and loamy soils (pH range 7–7.8), Fe contents vary from 100 to 200 $\mu\text{g/L}$, whereas in light acid sandy soils (pH range 2.5–4.5), Fe contents range from 1000 to 2223 $\mu\text{g/L}$.

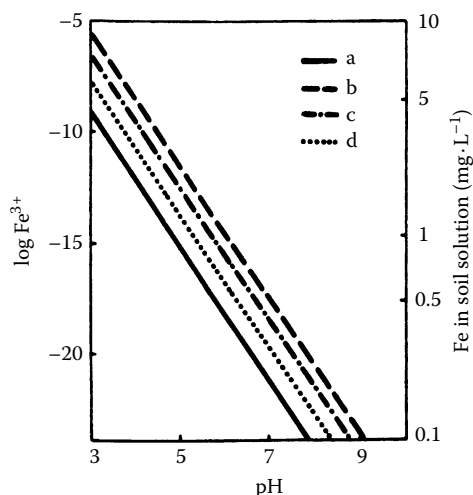


FIGURE 13.1 Influence of soil pH on the activity of Fe^{3+} maintained by Fe oxides. (a) $\alpha\text{-FeOOH}$, goethite; (b) $\text{Fe}(\text{OH})_3$, amorphous; (c) $\text{Fe}(\text{OH})_3$, soil constituent; and (d) Fe concentration in soil solution. (Data from Lindsay, W. L., *Chemical Equilibria in Soils*, Wiley-Interscience, New York, 449, 1979; Kabata-Pendias, A. and Wiacek, K., *Soil Sci. Ann.*, 36/4, 33, 1985.)

(Kabata-Pendias and Wiacek¹⁰⁸⁴). The ionic species of Fe commonly occurring in soil solutions are as follows:

Cationic forms: Fe^{2+} , FeCl^+ , $\text{Fe}(\text{OH})_2^+$, $\text{FeH}_2\text{PO}_4^+$.
 Anionic forms: $\text{Fe}(\text{OH})_3^-$, $\text{Fe}(\text{SO}_4)_2^-$, $\text{Fe}(\text{OH})_4^{2-}$.

The redox behavior of Fe in soils has been widely studied and described in several textbooks, and recently by Alloway,¹²⁰¹ Bartlett,¹²¹⁹ and Sparks (1995). In waterlogged soils, the reduction of Fe^{3+} to Fe^{2+} affected by both abiotic and biotic factors is resulted in an increase of its mobility. Also some factors, such as acid rain, acid fertilizers, and high input of OM, may control the Fe mobility in soils. Amounts of crystalline Fe oxides in soils irrigated with municipal wastewater are relatively high, within the range from 22% to 66% of the total Fe contents, whereas Fe species bound to Mn oxides were rather negligible, from 1% to 8% of the total Fe (Kabała and Wilk, 2004). In consequence, geochemical and pedochemical Fe cycling associated with its mobility and phytoavailability may be significantly changed under anthropogenic impact.

Although soil Fe is slightly mobile under most soil conditions, it also exhibits a tendency to form mobile organic complexes and chelates. These compounds are largely responsible for the Fe migration between soil layers and for leaching of Fe from soil profiles; they are also important in the supply of Fe to plant roots. The budget of Fe in soils calculated as input–output differences indicates losses of Fe, mainly from soils under the spruce forest, and this phenomenon is particularly associated with acid and light soils (Table 3.13).

The soluble Fe level reaches a minimum in the alkaline pH range (Figure 13.1). Acid soils are therefore higher in soluble inorganic Fe than are neutral and calcareous soils. Thus, Fe^{2+} cations, when in acid anaerobic soils, may become toxic, but in alkaline well-aerated soils, the low concentration of soluble Fe species may not meet plant requirements for this metal. When soils are waterlogged, the reduction of Fe^{3+} to Fe^{2+} takes place and is reflected in an increase in Fe solubility. This process of Fe reduction is strongly related to metabolism of bacteria and can result in a high Fe^{2+} concentration in some submerged soils (e.g., paddy soils).

Areas of Fe deficiency in soils for certain crops are relatively widespread (Table 5.11), but most occur under aridic climates and are related to calcareous, alkaline, or other specific soils

(e.g., manganiferous soils). In the humid climatic zone with a predominance of acid soils, Fe deficiency in soils is most unlikely to occur unless anthropogenic factors disturb its natural cycling.

Soil testing and the correction of the Fe deficiency have been the subjects of several studies, and all authors have stated that caution should be used in formulating methods for determining plant-available levels of Fe.^{151,279,847} There is still a lack of suitable methods to assess the Fe availability to plants. The chelating agents DTPA and EDTA appear to be most often recommended for measuring the Fe phytoavailability. However, Kreijl et al.¹³⁷⁹ reported that the correlation between Fe in several substrate extracts (e.g., H₂O, EDTA, DTPA, and CaCl₂) and Fe in the test plant (chrysanthemum) was poor.

C PLANTS

1 Absorption and Transport

The mechanisms of Fe uptake and transport by plants have received much study because they are the key processes in the supply of Fe to plants. The present knowledge on this topic has been extensively reviewed by Moore,⁵⁴⁸ Chaney et al.,¹²⁸ Tiffin,⁷⁸⁹ Mengel and Kirkby,⁵³¹ and Tinker.⁷⁹⁸

Almost all instances of Fe deficiency in plants are considered to occur because of soil factors that govern the Fe mobility. Soil conditions that render Fe unavailability are summarized in Table 5.11. However, also plant metabolism controls Fe availability, apparently due to the differential mugineic acid secretions (Maruyama et al., 2005).

Main features of the Fe uptake by plants and Fe transport between plant organs may be summarized as follows:

- Various Fe species may be absorbed, mainly as Fe²⁺, but also Fe³⁺, and Fe chelates.
- Plant roots may reduce Fe³⁺ to Fe²⁺, which is fundamental in the Fe absorption by most plants.
- At Fe deficiency conditions, roots (especially of cereals and other *Gramineae*) release mugineic acids that are effective in mobilizing Fe.
- In xylem exudates, Fe occurs mainly in unchelated forms.
- The Fe transport is mediated largely by citrate chelates and by soluble ferritins (transferins).

At conditions of Fe deficiency, roots of some plants can develop various mechanisms responsible for enhanced Fe solubility through the reduction of Fe³⁺ and/or chelation in phytosiderophore forms that are efficient in mobilizing Fe (Marschner et al., 1989). Phytosiderophores released by the roots of *Poaceae* into the rhizosphere especially influence the availability and uptake of Fe and, probably, other metals (Reichman and Parker, 2005). Fe-humate complexes appeared to be a good Fe source for plants (Boganegra et al., 2004).

Both Fe uptake and transport between plant organs are highly affected by several plant and environmental factors. Soil Eh–pH status, concentration of Ca and P, and ratios of several trace metals are most pronounced. In general, a high degree of oxidation of Fe compounds, Fe precipitation on carbonates and/or phosphates, and competition of trace metal cations with Fe²⁺ for the same binding sites of chelating compounds are responsible for a low Fe uptake and for a disturbance in Fe transport within plants. Usually, at higher Fe deficiency, greater ability of plant roots to extract Fe from minerals and from chelating agents.

2 Biochemical Functions

The metabolic functions of Fe in green plants are relatively well-understood, and Fe is considered the key metal in energy transformations needed for syntheses and other life processes of the cells.^{83,564,630,1184} The essential role of Fe in plant biochemistry may be summarized as follows:

- Several Fe-proteins, mainly transferrins, ferritins, and siderophores, are involved in transport, storage, and binder systems.

- Fe occurs in hem and nonhem proteins and is concentrated mainly in chloroplasts.
- Chlorophyll formation is influenced by Fe.
- Organic Fe complexes are involved in the mechanisms of photosynthesis electron transfer.
- Nonhem Fe proteins are involved in the reduction of nitrites and sulfates.
- Fe is directly implicated in the metabolism of nucleic acids.
- Both cations, Fe^{3+} and Fe^{2+} , may also play a catalytic role in various reactions.

This summary is oversimplified and too generalized, but it gives some information showing that, in addition to the active Fe roles in redox reactions of chloroplasts, mitochondria, and peroxisomes, Fe also performs other functions in plants.

Iron deficiency affects several physiological processes and therefore retards plant growth and plant yield. The deficiency of Fe is a major worldwide problem with many crops since a large number of cultivated soils are low in its available content. The control of Fe deficiency often is not sufficiently effective and therefore much effort has been made in screening plants for iron efficiency. Brown^{104a} reviewed the current approach to the Fe deficiency problem and stated that genotypes and plant species should be selected for their efficient absorption of Fe.

The symptoms of Fe deficiency may occur at very different Fe levels in plants, and this deficiency is highly dependent on soil, plant, as well as on nutritional, and climatic factors. The most common initial symptom of Fe deficiency is interveinal chlorosis of young leaves (Table 5.10). Several fruit trees and, of all cereals, oats, and rice in particular, are very susceptible to Fe chlorosis.

On soil rich in mobile Fe fractions, an excessive Fe uptake can produce toxic effects in plants. Plant injury due to Fe toxicity is most likely to occur on strongly acid soils (Ultisols, Oxisols), on acid sulfate soils, and on flooded soils. High concentrations of Fe in the soil solution is almost always related to Fe toxicity. This toxicity is also often associated with salinity and a low phosphorus or base status of soils. It was reported for countries of both tropical and arid regions.⁶²² The concentration of Fe^{2+} at about 500 mg/kg in paddy soils was reported to kill rice seedlings.²⁴¹ It should be emphasized that both an excessive Fe uptake and a low tolerance to a high concentration of Fe in plant tissues is significantly complicated by several nutritional factors.

Symptoms of Fe toxicity are not specific and usually differ among plant species and stages of growth (Table 5.8). Injured leaves or necrotic spots on leaves indicate an accumulation of Fe above 1000 mg/kg (3–6 times as high as the Fe content of healthy leaves). However, the most pronounced symptom is the ratio of Fe to other macro and trace elements. The proper Fe:Mn ratio seems to be the most obligatory factor in the tolerance of plants to Fe toxicity.

The physiology of Fe toxicity and of plant resistance to the excess of this metal can be summarized as follows:

- Plants high in nutrients, especially in Ca and SiO_2 , can tolerate increased levels of Fe.
- Roots (especially of rice) are able to oxidize Fe and deposit it on root surface.
- Mycorrhizas reveal a great capability to bind Fe either at the root surface or in root cells.
- Root damage by various factors destroys the oxidizing power of roots and aggravates Fe availability and thus Fe toxicity.
- Plant resistance to excess Fe is associated with different reactions like oxidation, immobilization, and exclusion of mobile Fe forms by roots.
- Plants adapted to waterlogged conditions are commonly more tolerant to high Fe levels than plants grown in well-aerated soils.

Iron tolerance of plants is most often associated with oxidation and immobilization and/or exclusion of soluble Fe by roots. Plant response to Fe toxicity, as well as to Fe deficiency, is highly variable among genotypes and plant species. Therefore, genetic manipulation through plant breeding seems to be one of the most promising lines of research on the Fe problem in plant nutrition.

3 Interactions with Other Elements

Interactions between Fe and other trace and major elements are very complex and may occur within plants as well as at the root surface. In most cases these are antagonistic interrelationships, and can be presented as follows:

- Excess amounts of Mn, Ni, and Co cause a reduction in the absorption and translocation of Fe that resulted in a decrease of chlorophyll.
- High levels of Fe compounds in growth media result in decreasing uptake of several trace metals, mainly of Mn, Ni, and Co.
- Interactions between Fe and Mn in both growth medium and plant tissues have the most important impact on plant metabolism. The ratio of these two metals in both growth media and plant tissue seems to be more important to plant metabolism than their concentrations.
- The interaction of Fe–Zn seems to be associated with the precipitation of franklinite, ZnFe_2O_4 that depresses the availability of both metals.
- Antagonistic interactions between Fe and Si, and Se have been observed.
- Fe–P interactions, in both plants and soils, are related mainly to the precipitation of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$. Furthermore, P anions compete with plants for Fe and interfere with Fe uptake and its transport. The appropriate P:Fe ratio is fundamental to plant health.
- In K-deficient plants, Fe may become toxic due to disrupted oxidation of Fe^{2+} to Fe^{3+} .
- Fe–Ca interactions, in both plant and soil, are very complex, but the significant impact of Ca is to suppress Fe availability, and thus may lead to Fe chlorosis in plants on calcareous soils.
- Fe–S interactions cause a low Fe availability at low soil S, whereas a high S content may also result in a low Fe solubility, depending on soil environments.

The interaction between Fe and Cd observed in phytosiderophores is complex and contributes to the Cd tolerance of a plant (Meda et al., 2007). Both, Cd and Zn, interfere in Fe binding in spinach biomass (Pavliková et al., 2002). The negative correlation between Se content of cereal grains and Fe in soils is suggesting a possible immobilization of Se by Fe minerals/compounds (Johnson et al., 2000). Antagonistic interaction between Fe and trace metals has been observed in several crops, and results of several studies suggest that chlorosis brought by trace metal excess is apparently the result of induced Fe deficiency.^{16,105,778}

4 Concentrations in Plants

The appropriate content of Fe in plants is essential both for the health of plants and for the nutrient supply to man and animals. The variation among plants in their ability to absorb Fe is not always consistent and is affected by changing conditions of soil and climate and by stages of plant growth. Generally legumes are known to accumulate more Fe than other plants. However, where Fe is easily soluble, plants may take up a very large amount of Fe. This is clearly shown by vegetation grown in soils derived from serpentine, where grass contained Fe within the range of 2127–3580 mg/kg.³⁶⁶

The natural Fe content of fodder plants ranges from 18 to about 1000 mg/kg (Table 13.3). The nutritional requirement of grazing animals is usually met at the Fe concentration range from around 50 to 100 mg/kg in forage.

Edible parts of vegetables contain Fe within mean values from 33 to 65 mg/kg, in carrot and soybean seeds, respectively (Table 13.4). Various cereal grains do not differ much in their Fe concentrations. The average Fe contents of different cereals range from 31 to 98 mg/kg. Values above 100 mg/kg are reported only for some countries, for example, 218 and 133 mg/kg, in barley from the United Kingdom and in oats from Canada, respectively.

TABLE 13.3
Iron Concentrations in Grass and Clover at the Immature Growth Stage from Different Countries (mg/kg)

Country	Grasses		Clovers		Reference
	Range	Mean	Range	Mean	
Australia	228–264	244	252–357	285	266
Great Britain	73–154	103	122–132 ^a	—	867a
Finland	39–49	43 ^b	—	—	388
Germany	79–206	126	116–253	175	31
Germany	110–430	187	—	—	596
Hungary	133–923	376	118–535	346 ^c	803
Ireland	34–78	55	64–85	74 ^a	235
Japan	55–157	106	75–229	152	770
Poland	60–140	92	76–136	117	838
U.S.	18–320	73	—	—	200
New Zealand	69–1510	320	105–1700	400	536

^a Alfalfa.

^b Timothy.

^c Various legumes.

II RUTHENIUM

A INTRODUCTION

Ruthenium is a member of the group of platinum metals and is considered to be the least abundant of metals of this group. Its mean concentration in the Earth's crust is estimated at 1 µg/kg (Table 3.2), whereas its contents in rocks vary from 0.01 to 60 µg/kg. Its mean background value for soil is established as 0.1 µg/kg (Fritsche and Meisel, 2004).

The occurrence of Ru is often associated with Os and Ir, as well as with some base metals such as Fe or Cu. Some sulfide (e.g., laurite, RuS₂) and arsenosulfide minerals of Ru were recently found at very low concentrations in other sulfide and arsenosulfide minerals (Fairbridge, 1972). Naturally occurring isotopes are mainly ¹⁰²Ru and ¹⁰⁴Ru.

The deposits of Ru are closely associated with Pt and Pd. Pure Ru is a very hard metal and not subject to attack by acids, but reacts with alkalis, especially under oxidizing conditions. Like other PGMs, Ru does not easily combine with trace elements. This metal is extracted mainly at the refinery of Ni and Cu. It is used as a hardener for Pt and Pd alloys and to increase the resistance to corrosion of some other metal alloys. It is also used as a substitute for Pt in jewelry. Ru is used in some electronic devices and for special ceramic paints, optical instruments, and glass of a required quality. This metal exhibits catalytic properties in the synthesis of some hydrocarbons.

B SOILS AND PLANTS

Ruthenium content in soils and cereal grains of Sweden is (in µg/kg) <40 and <1, respectively (Eriksson, 2001). Its aerial deposition in Sweden was calculated at <11 mg/ha/year. In soils along motorways, Ru concentrations vary from 0.01 to 5.77 µg/kg (Fritsche and Meisel, 2004). Elevated contents of ¹⁰⁶Ru were found in bottom sediments of Danube River, below the nuclear reactor (Pavlotskaya⁶⁰³).

TABLE 13.4
Iron in Plants Grown in Various Countries^a (mg/kg)

Plant	Range	Mean
Wheat, grains	17–50	31
Rye, grains	34–43	38
Barley	33–218	98
Oats, grains	54–140	93
Bean, pods ^b (FW)	17–89	46
Soybean seeds ^c	48–81	65
Carrot, roots	16–67	33
Onion, bulbs	33–50	34
Beet, roots	71–82	77
Potato, tubers	21–58	40
Potato, tubers ^b (FW)	3.4–4.0	3.7
Strawberry, fruits ^b (FW)	2.7–3.7	3.1
Nuts and almonds ^d	9–67	15
Sunflower, fruits ^e (FW)	1–11	—

^a Presented are worldwide values from various sources, unless otherwise stated.

^b After Szteke B., Jędrzejczak R. and Ręczajska W. 2004. *Ann. Nat. Inst. Hygiene*, Suppl. 55:21–27 (in Polish), data for Poland.

^c After Moraghan J.T. and Helms T.C. 2005. *J. Plan Nutr.* 28:1453–1463.

^d After Jędrzejczak R. 2004. *Ann. Nat. Inst. Hygiene*, Suppl. 55:13–20 (in Polish), from markets in Poland.

^e After Enslinger A.H., et al. 1995. *The concise encyclopedia of foods and nutrition*, 2nd ed. CRC Press, Boca Raton, FL, data for the United States.

Some studies on ^{106}Ru behavior of in soil show that this radionuclide is largely accumulated in surface soil layers (Handl, 1988). In acid soils, however, ^{106}Ru is highly mobile and is likely to migrate down the soil profile.¹⁷ Also Schimmack et al.¹¹⁴⁰ reported that this radionuclide is mobile in soil.

The radionuclides, ^{103}Ru and ^{106}Ru , are released during nuclear reactions. Both radionuclides, and particularly ^{106}Ru , were deposited on soil by the fallout after the Chernobyl accident.

Bowen⁹⁴ reported Ru to occur in land plants at the concentration of 5 $\mu\text{g/kg}$. Duke¹⁹⁷ reported Ru in food plants from a Central American tropical forest region to range from 0.4 to <200 $\mu\text{g/kg}$. Plants exposed to automobile exhausts contain Ru in the range of 0.3–0.9 $\mu\text{g/kg}$, with the highest value for moss and the lowest for mushrooms (Djingova et al., 2003). The concentrations of both radioisotopes, ^{103}Ru and ^{106}Ru , in the lichen (*Stereocaulon vesuvianum*), sampled in Italy in autumn 1986, indicated an increase with elevation of Mt. Vesuvius, from 90 to 110 Bq/kg and from 320 to 520 Bq/kg, respectively (Adamo et al., 2004).

Plants relatively easily take up the ^{106}Ru radionuclide, but a large proportion is concentrated in roots. According to Grogan et al.¹⁰¹⁶ this radionuclide is not likely to be easily transferred from soil to the food chain, however, under specific conditions it might be significantly increased in plants. Handl (1988) observed considerable differences in the uptake of ^{106}Ru by plants from two applied compounds: nitrosyl and chloride. Willey and Fawcett (2006) reported that there is a significant phylogenetic effect on uptake and concentration of $^{103/106}\text{Ru}$ in plants.

III OSMIUM

A INTRODUCTION

Osmium is a member of the PGMs, but in contrast to other metals of this group, it does not concentrate preferably in the nickel–iron phase of chondrites. This metal is notable for its great density (Table 13.1). Its abundance in the Earth's crust is calculated at 0.5 µg/kg (Table 3.2). Like other PGMs, Os occurs mainly in native alloys of variable composition. Unlike other PGMs, Os easily reacts with oxygen and may occur at various oxidation states, from +3 to +8 (Table 13.1), and also may have –1 oxidation state. There are no Os minerals, but this metal is likely to be associated (at about 3%) with laurite (Ru,Os)S₂. Some other mineral species of PGMs exhibit an affinity for increased amounts of Os, up to about 30% (e.g., iridosmine, and osmiridium—native alloys of variable composition).

There are seven stable isotopes of Os. This metal is resistant to acids but is susceptible to reactions with alkalis. There is a small production of Os, estimated as 300 tons/year in 1995 (Reimann and de Caritat, 1998). The metal is used mainly for the production of hard-wearing alloys and for electronic devices. During metal processing, various Os compounds are formed, such as, OsF₆, OsCl₄, and volatile OsO₄.

All Os compounds are toxic to humans and animals, and can cause lung congestion, skin damage, and severe eye damage. Longer exposure to increased levels of some Os compounds is hazardous to marrow, liver, and kidneys.

B SOILS AND PLANTS

Background Os content in soils was estimated by Fritsche and Meisel (2004) as 0.05 µg/kg, that is the same as in the Earth's crust (Table 3.2).

There is not much information on Os contamination, even in the vicinity of likely sources of Os pollution. However, Os is known to be released to the environment as a volatile tetroxide (OsO₄) during metal processing. Also Os emitted from automobile catalytic converters is accumulated in soils. In soils along motorways, Os concentrations vary between 0.03 and 2.36 µg/kg (Fritsche and Meisel, 2004). Values of isotopes ¹⁸⁷Os:¹⁸⁸Os ratio in environmental samples are used to differentiate local Os sources (Rodushkin et al., 2007).

Soluble Os⁴⁺ species are easily mobile and thus may be available to plants and are relatively toxic (Smith et al.⁷⁴³ Farago and Parsons, 1994). Although Os is considered as metal biologically unreactive, its increased content in food and fodder plants might be of a great health risk.

14 Elements of Group 9 (Previously Part of Group VIII)

The elements of Group 9 are cobalt (Co), rhodium (Rh), and iridium (Ir). Co belongs to the iron family metals, which includes also Fe and Ni, previously in the Group VIII. Rh and Ir are noble metals of the platinum group (PGMs). According to the IUPAC recommendation, these elements belong to the Group 9. All three metals exhibit variable properties, siderophilic and/or lithophilic characters, and variable oxidation states (Table 14.1).

I COBALT

A INTRODUCTION

Cobalt, in the Earth's crust, is highly concentrated in mafic rocks, up to 200 mg/kg, when compared to its content in acid igneous rocks, 1–15 mg/kg, and to its abundance in the upper continental crust, 10–12 mg/kg (Table 14.2). It is also likely to concentrate in black shales.

As Co reveals siderophilic character it is likely to form minerals with S, As, and Se. Its common rock-forming minerals are: cobaltite, CoAsS ; smaltite, CoAs_{2-3} ; linneite, Co_3S_4 ; and arsenosulfide, CoAsS . In the hypergenic zones and in soils, the formation of erythrite, $\text{Co}_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ is likely to occur. In ground water and desert varnish occurs birnessite, a mineral oxide of complex formula composed of Mn, Ca, K, and Na.

The geochemical cycle of Co closely resembles that of Fe and Mn cycling, and is likely to be associated with several minerals of these metals. During weathering processes, Co^{3+} is unstable in the aqueous phase and precipitates as sulfides and/or adsorbed by hydrous oxides. In soils, however, Co behavior seems to be strongly influenced mainly by the Mn oxide phase formation. The absorption capacity of Co by Mn oxides, of both biogenic and abiogenic origin, is very high (Tani et al., 2003). Relatively easy interactions of Co with all metals that are associated geochemically or biochemically with Fe, have a significant impact on its behavior in soils and its phytoavailability.

Global mining of Co in 2009 was 71.8 kt (USDI, 2009). Most of Co is used for special alloys utilized in several industries. It is also used in chemical catalyses and synthesis, as well as a plastic hardener. In pharmacy Co is used for medical and veterinarian drugs. The radionuclide ^{60}Co is applied for some medical treatments.

B SOILS

The Co content of soils is inherited mainly from parent materials. The worldwide mean value of Co in surface soils is calculated as 10 mg/kg (Table 3.2). Usually, higher levels of Co are in heavy loamy soils (Cambisols) and, sometimes, in organic soil (Histosols) (Table 14.2).

The content and distribution of Co in soil profiles are dependent on soil-forming processes and therefore differ for soils of various climatic zones. Higher Co contents of surface soils are found in arid and semiarid regions, for example, Egyptian soils contain Co from 16.5 to 26.8 mg/kg (Nasseem and Abdalla, 2003), while low soil Co has been reported for the glaciated regions of northern parts of different continents, as well as for the Atlantic Coastal Plain of the United States. Light soils developed from glacial deposits under temperate humid climate usually contain small quantities of Co. Thus, median value for Co in Lithuanian soils is reported to be 3.4 mg/kg, and in soils of the northern

TABLE 14.1
Selected Properties of Trace Elements of Group 9

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C, g/cm ³)	Valence ^b
Co, cobalt	27	58.93	167	8.9	+2, +3, +4
Rh, rhodium	45	102.9	183	12.4	+2, +3, +4, +6
Ir, iridium	77	192.2	187	22.4	+2, +3, +4, +6

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for main oxidation states.

region of Russia is 5.5 mg/kg.¹³⁵⁷ Swedish arable soils contain Co in the range of 0.4–14 mg/kg, at the average value of 7.1 mg/kg (Eriksson, 2001). Surface horizons of Russian chernozems contain Co in the range of mean values from 9.2 to 10.8 mg/kg (Protasova and Kopayeva¹¹²³). Co contents in soils of South Africa range from 1.51 to 68.5 mg/kg, with median value 8.44 and arithmetic mean 18.0 (Herselman et al., 2005). Naturally high Co contents are observed in soils over serpentine rocks, up to 520 mg/kg (Table 14.3), and in soils around ore deposits, up to 85 mg/kg. The range of Co in reference soil samples of the United States is from 5.5 to 29.9 mg/kg and in Chinese soils, in the range of 5.5–97 mg/kg.¹³¹³ Soils over mafic rocks and soils derived from clay deposits contain the highest amounts of this metal. Other high Co concentrations reported for Australian ferralsols (122 mg/kg) and Japanese soils (116 mg/kg) are related either to pollution or to specific enrichment.¹³⁵⁷

Several soil factors govern the Co distribution in soils. However, hydrous oxides of Fe and, Mn are of the greatest importance. Both, Fe and Mn oxides are known to have a great affinity for selective adsorption of Co. This was observed in most kinds of soils and is reflected in the Co distribution in soil profiles showing a general similarity between the levels of Fe and Co in soil horizons. Amounts of Co are always higher in the B-soil horizons where Fe is concentrated (Figure 14.1). However, in certain soils enriched in Mn minerals, the association of Co with Mn dominates other

TABLE 14.2
Abundance of Co in Rocks and Soils (mg/kg)

Rock/Soil	Co
Earth's crust	9–12
Igneous rocks	—
Mafic	35–200
Acid	1.0–15
Sedimentary rocks	—
Argillaceous	14–20
Sandstones	0.3–10
Calcareous	0.1–3.0
Soils ^a	8
Arenosols (sandy)	0.8–12
Podzols (medium loamy)	4–65
Cambisols (heavy loamy)	5–58
Calcisols (calcareous)	1–70
Histosols (organic)	0.5–50

^a Soil groups are given according to the WBR (Table 3.1).

TABLE 14.3

Cobalt Enrichment and Contamination in Surface Soils (mg/kg)

Site and Pollution Source	Mean or Range of Content	Country	Ref.
Soil over serpentine rock	10–520	New Zealand	495
Mining or ore deposit	13–85	U.S.	744
Metal-processing industry	10–127	Canada	150, 333
	18	Germany	390
	67	Great Britain	1005
	20–70	Norway	441
	42–154	U.S.	744
Sludged farmland	3.3–12.4	Holland	314
Roadside or airport area	7.9	U.S.	744
Urban street dusts	6–14	Great Britain	744

factors governing the Co distribution. Fe nodules may accumulate Co up to 300 mg/kg, Fe–Mn concretions contain Co within the range of 70–390 mg/kg, and Mn-rich points of soil may concentrate above 20,000 mg/kg (Table 4.3).

Cobalt speciation in soils depends on several factors, among which the Eh potential plays a significant role. Both the reduction of soil Eh and the decrease in soil pH may result in the solubilization of precipitated or adsorbed Co. The oxidation of Co^{2+} to Co^{3+} , especially by Mn oxides, is a common process in soils. Interchange reactions are involved in the sorption of Co by Mn oxides, leading to the formation of hydroxyl species, $\text{Co}(\text{OH})_2$ that precipitated at the oxide surface. Different redox mechanisms have been proposed for the sorption of Co by Mn oxides. In general, these include: (1) oxidation of Co^{2+} to Co^{3+} at the oxide interface, (2) reduction of Mn^{4+} to Mn^{3+} in the oxide crystal lattice, and (3) replacement of Mn^{4+} or Mn^{3+} by Co^{3+} (Fleming⁹⁹⁷). In soils, the sorption of Co by Mn and Fe minerals increases greatly with pH and also is controlled by redox soil potential (Figure 14.2). Roles of montmorillonitic and illitic clays especially are cited by numerous investigators as being of significance because of their great sorption capacity and their relatively easy release of Co. In sludge Co is associated with carbonates, OM, S, and residual

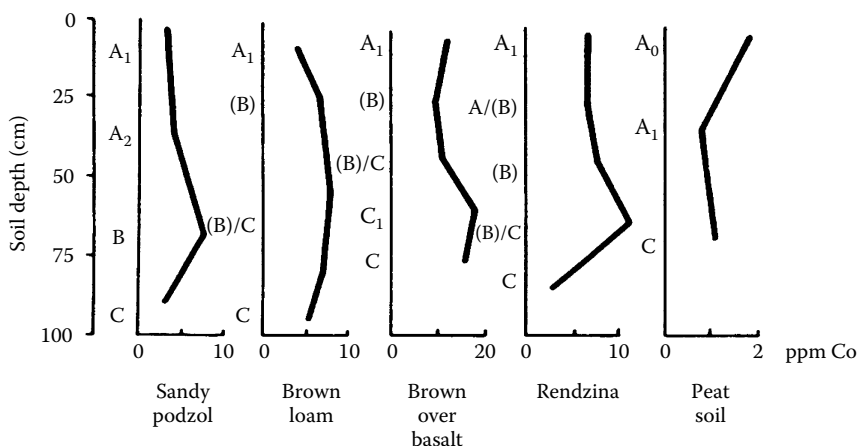


FIGURE 14.1 Distribution of Co in the profiles of different soils developed under humid climate conditions. (Letters indicate genetic soil horizons.)

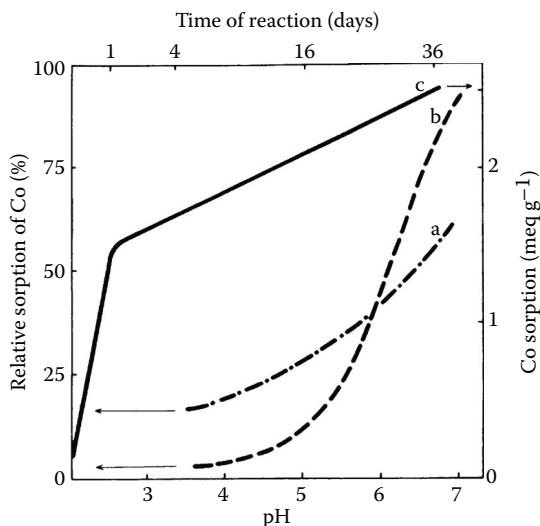


FIGURE 14.2 Effects of pH on the sorption of Co by (a) Mn nodules and (b) goethite and effects of time on the sorption of Co by (c) birnessite. (From McKenzie, R. M., *Trace Elements in Soil–Plant–Animal Systems*, Academic Press, New York, 83, 1975. Copyright Elsevier 1975. With permission.)

fractions. Antagonistic interactions between Co and Ni, Cu, Zn, Ca, and Fe was observed in sludge (Begona Osuna et al., 2004).

Soil texture and SOM play an important role in the Co behavior in soils. The impact of SOM is variable and depends on the kind of OM and pH. Although soils rich in OM usually have low Co contents, an increased level, up to 50 mg/kg, was for some Chernozems.¹¹²³ Several organic ligands stimulate the sorption of Co on Fe-coated silica compounds, but increase the Co mobility when Fe hydroxides are absent.^{1244a} The mobility of Co is strongly related to kind of SOM. Organic chelates of Co are known to be easily mobile and translocated in soils.

In most soils, Co is rather slowly mobilized and thus its concentrations in soil solution range from 0.3 to 87 µg/L. Common ionic species occurring in soil solutions are: Co^{2+} , Co^{3+} , CoOH^+ , and $\text{Co}(\text{OH})_3^-$. Also complex compounds, such as $\text{Co}(\text{OH})_2^0$, of a relatively high stability constant, may occur in soil solution (Kabata-Pendias and Sadurski, 2004).

An adequate supply of Co to grazing animals (especially ruminants) has been for years of a great challenge. Acetic acid-soluble and EDTA extractable Co usually corresponds to the readily available pool of the metal. Pasture soils, of the texture of loamy sands and clays, from the North Western Coast of Egypt contain the AAAC-EDTA extractable Co from 3.60 to 4.69 mg/kg (Nasseem and Abdalla, 2003). The authors suggested that an extractable Co content less than 2.45 mg/kg in pasture soils may cause a deficiency of Co in animals. The application of Co sulfate compounds or EDTA chelates to soil are the most common practices in controlling the Co deficiency in ruminants.

There is some evidence of Co enrichment in contaminated soils. In surface soils around metal processing industries, Co can reach up to 154 mg/kg.⁷⁴⁴ Some increase in Co contents was also observed in sludged farm soils as well as in roadside soils (Table 14.3).

Factors contributing to Co deficiency for grazing animals are associated mainly with alkaline or calcareous soils, light leached soils, and soils with high OM content (Table 5.7). The Co content and distribution in soil profiles are also dependent on the soil-forming processes and therefore differ for soils of various climatic zones. Usually, higher Co contents of surface soils are observed for arid and semiarid regions, whereas exceedingly low soil Co is reported for light soils of the Atlantic Coastal Plain and for soils of the glaciated region of the northeastern United States.⁴³⁶

Significant sources of Co pollution are related to nonferrous metal smelters, whereas coal and other fuel combustions are of considerably less importance. Roadside soils and street dusts usually are enriched in Co (Table 14.3).

C PLANTS

1 Absorption and Transport

Contents of Co in plants are highly controlled by both soil factors and the ability of plants to absorb this metal. In higher plants, absorption of Co^{2+} by roots involves active transport. However, in the xylem, the metal is mainly transported by the transpiration flow. Co complexing with organic compounds controls its bioavailability. A low mobility of Co^{2+} in plants restricts its transport from stems to leaves.

Cobalt in nutrient or soil solution is easily available to plants. Co species soluble in AAAC-EDTA extractants are highly correlated with its levels in crop plants.¹⁴⁹¹ Bhattacharya et al. (2008a) reported that Co bound to Fe and Mn oxides of both municipal solid waste compost (MSWC) and cow dung manure (CDM) is relatively easily uptaken by rice, whereas Co occurring in carbonate, OM and residuals fractions of MSWC and CDM does not correlate with its contents in rice straw and grains.

Numerous studies have been made on plant uptake of Co from soils, and it has been shown that enrichment of a soil with Co increases its levels in plants. The Co uptake by plants is a function of content of its mobile fractions and of the Co concentration in solution (Figure 14.3). During absorption, Co behaves like other trace metals (e.g., Fe, Mn) and is transported in forms bound to complexing organic compounds with a molecular weight in the range of 1000–5000, with a negative overall charge.⁸⁷² Apparently, the simultaneous transport of Co^{2+} (like Fe^{2+}) with citrate cannot be precluded. Co is easily taken up by leaves through the cuticle; therefore, foliar applications of Co in solution are known to be effective in the correction of Co deficiency. Liming and different fertilizers influence the solubility of Co. As Klessa et al.¹³⁶⁵ suggested, liming is a major factor in reducing Co phytoavailability. This creates a risk of a low Co content of fodder plants, which affects a dangerous Co deficiency in ruminants.

2 Biochemical Functions

The essentiality of Co for both blue-green algae and microorganisms in fixing N_2 is now well-established. In lower organisms, Co inhibits tetrapyrrole biosynthesis. It is not clear, however,

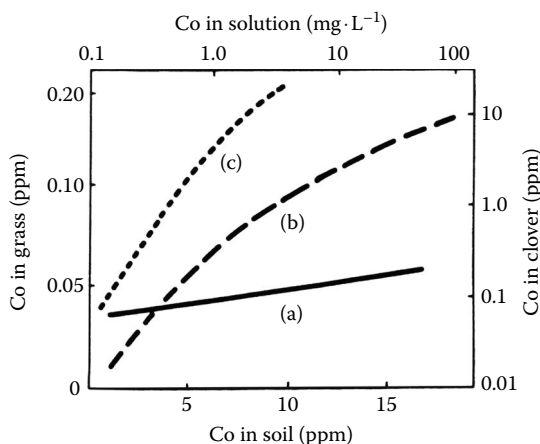


FIGURE 14.3 Co uptake by plants from soil or nutrient solution. (a) Ryegrass grown on soil; (b) clover, tops, grown in culture solution; (c) clover, roots, grown in culture solution. (Data from Coppenet, M., et al., *Ann. Agron.*, 23, 165, 1972; Kabata-Pendias, A. and Wiacek, K., *Soil Sci. Ann.*, 36/4, 33, 1985.)

whether Co is essential for higher plants, although there are some evidences that it participates in chlorophyll formation. There is also some evidence of a favorable effect of Co on plant growth and especially on N-fixing processes (Jagodin et al.,³⁴⁹ Mengel and Kirkby,⁵³¹ Reisenauer et al.,⁶⁴⁸ and Palit et al., 1994). The role of Co in the photosynthesis is controversial. Low concentration of Co stimulates growth of both algae and higher plants. However, relatively higher concentrations are toxic. Co is not found at the active sites of any respiratory chain enzymes although it is involved in mitochondrial respiration. Co is a component of vitamin B₁₂ and cobamide coenzyme, and thus is involved in the fixation of N₂ in root nodules of legumes. However, this metal inhibits the metabolism of cyanobacteria that controls the N₂ fixation (Palit et al., 1994).

Smith and Carson⁷⁴⁴ compiled information from several sources on the effects of Co on nonlegumes, and the final opinion is inconclusive. Although traces of Co coenzymes have been detected in nonlegumes, it is not known whether these compounds might have originated from microorganisms associated with the plant.⁵⁶⁴ Beneficial effects of low Co concentrations on plant metabolism are not yet fully understood. Presumably, several effects are cross-linked with interactions with other trace metals.

In legumes and alder (*Alnus* sp.), Co affects the ability of plants to fix N₂ from air. Co is chelated at the center of a porphyrin structure termed the cobamide coenzyme, which is effective in the N₂ fixation. Nicholas⁵⁶⁴ reviewed all recent findings on the Co function in N₂ fixation and stated that cobamide coenzymes are involved in the migration of the H atom during the formation of the NH₃ compound by rhizobia. Although Co is known to be essential in certain bacterial functions, it is also reported to inhibit Mg uptake by some microorganisms and to exhibit antimicrobial activity.⁸⁵⁶

Cobalt deficiency inhibits the formation of leghemoglobin in legumes and hence the N₂ fixation. However, the Co requirement for this process is low. As Wilson and Reisenauer⁸⁸³ stated, as low concentration of Co as 10 µg/L in the nutrient solution was adequate for the growth of alfalfa. In natural conditions, Co deficiency is not known to retard the growth of either nonlegumes or legumes. Co deficient plants develop more lateral nodules but fewer crown nodules, than normal plants and the N₂ fixing ability of the deficient plants improved throughout the growth period (Riley and Dilworth, 2006).

In fodder plants Co deficiency is considered mainly from the viewpoint of ruminant requirements since it is the component of a precursor of vitamin B₁₂. It has been observed that soils with a Co content of less than 5 mg/kg may produce herbage that is Co-deficient for the normal growth of animals. The critical Co level for ruminant diets is around 0.08–0.1 mg/kg, and similar levels were found in clover from different countries (Table 14.5). The deficiency of Co can be controlled by the application of Co salts to the soil, and the effect of such a treatment is known to last for several years.^{544,649} There are differences of opinion, however, as to whether it is better to apply Co to the soil or give directly to livestock when curing a Co deficiency. If a soil contains large amounts of Mn or Fe oxides capable of immobilizing Co, a shorter effective period should be expected. Case et al.¹²³ proposed that the Co content of fodder plants should not exceed 60 mg/kg because of the animal health hazard.

When Co is taken up in excess by roots, it principally follows the transpiration stream, resulting in an enrichment of Co at the leaf margins and tips. Therefore, the common symptoms of Co toxicity are white, dead margins and tips of leaves (Table 5.12). However, the primary reaction of plants to an excess of Co is interveinal chlorosis of new leaves, which is closely linked with Fe chlorosis. Cytological effects of Co excesses were reported to be inhibited mitosis and chromosome damage, or damage to the endoplasmic reticulum of root tips, and as disorganized phloem of the minor veins.^{643, 744}

In nature, although plant species range widely in their content of Co, toxicity symptoms are not often observed. When a high Co level is readily available, in polluted soil in particular, it can seriously affect plant growth and metabolic functions. Kitagishi and Yamane³⁹⁵ reported that the addition of 25 and 50 mg/kg of Co to the soil was toxic to rice plants. Anderson et al.²³ found the Co concentration of 140 mg/L in a soil solution from serpentine soils where oat plants were affected by the Co toxicity.

Different concentrations of Co in plant tissues have been reported to produce toxicity symptoms, as follows (in mg/kg): 43–142 in bush beans;⁸⁴¹ 19–32 in Sudan grass;²⁷⁹ and 6 in barley seedlings.¹⁷¹

Kloke et al.¹⁰⁵² gave a similar range of Co as toxic to sensitive plant species. However, commonly reported critical Co levels in plants range from 30 to 40 mg/kg.¹⁰⁸¹

Cereals are known as the most sensitive plants to the Co excess, but Anderson et al.²³ observed that toxic effects at Co concentrations of 10–20 mg/kg are most probably associated with an excess of Ni. As Palit et al. (1994) reported, Ni overcomes the inhibitory effect of Co on moss growth, indicating an antagonistic relationship.

The interaction of Co with other metals depends mainly on their concentrations. For example, high levels of Co induce Fe deficiency in plants and suppress uptake of Cd by roots. It also interacts synergistically with Zn, Cr, and Sn. In general, Co interacts with all metals that are associated biogeochemically with Fe (Tables 3.5). However, the most significant relationship has been observed between Co and Mn or Fe in plants. Both geochemical and biochemical antagonisms between these metals have arisen from their affinity to occupy the same sites in crystalline structures and from the similarity of their metallo-organic compounds. Increased salinity and Co content decrease chlorophyll content in some leaves (upper) of tomato plant. Levels of some plant hormones (e.g., auxins, gibberelins) also were controlled by Co and salinity (Gad, 2005).

3 Concentrations in Plants

In addition to soil factors highly controlling Co levels in plants, the ability of plant species to absorb this metal varies considerably. Its contents of food plants (Table 14.4) are of a nutritional importance to human and animals. Legumes are known to accumulate more Co than do grasses. Mean Co contents of clovers from various countries range from 100 to 570 µg/kg, whereas these values for grasses are between 60 and 270 µg/kg (Table 14.5).

The relatively large variations in Co levels, as reported by different authors for cereals and food plants, apparently reflect the impact of various factors, among which plant genotypes and environmental conditions play significant roles. Sillanpää and Jansson¹⁴⁹¹ evaluated results of analysis of wheat (before shooting stage, $N = 1723$) and of corn (6-leave stage, $N = 1892$) from 30 countries, and stated that soil texture is the most significant parameter controlling the Co level in plants. Mean values of Co in cereal grains, in the range of 5–270 µg/kg, show that its lowest concentrations are in cereals from Norway and the highest in cereals from Egypt (Table 14.4). Contents of Co in plant foodstuffs vary from 8 to 170 µg/kg, being the lowest in apples.

TABLE 14.4
Cobalt in Food Plants Grown in Various Countries^a (µg/kg)

Plant	Range	Mean
Wheat, grains (Norway)	1.5–14	4.7
Wheat, grains (Sweden)	1.1–18	4.5
Wheat, grains (Australia)	13–231	82
Wheat, grains (Egypt)	160–380	270
Barley, grains	4.4–44	18
Oats, grains	10–300	96
Cabbage, leaves	100–160	—
Carrot, roots	37–120	—
Onion, bulbs	28–80	—
Tomato, fruits	62–20	—
Cucumber, fruits	87–170	—
Potato, tubers	37–160	—
Apple, fruits	8–16	—
Orange, fruits	19–45	—

^a Values presented are compiled from various sources.

TABLE 14.5
Cobalt in Grass and Clover at the Immature Grown Stage from Different Countries^a (µg/kg)

Country	Grasses		Clover	
	Range	Mean	Range	Mean
Australia	–	–	70–530	190
Great Britain	<30–100	270	60–1700	570
Finland	40–80	60	–	–
Germany	30–220	90	60–210	120
Sweden	10–400	60	80–300	150
Japan	10–510	120	20–750	200
Poland	10–240	80	50–260	100
New Zealand	30–150	80	–	–
U.S.	<40–390	80	150–270	190

^a Values from various sources as compiled by Kabata-Pendias A., Pendias H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 400, 1999 (Po).

Plants are known to accumulate large amounts of Co and to develop a mechanism of Co tolerance which is basically similar to that occurring in any metalliferous plant species. Several plant species, mainly of the families *Cruciferae*, *Caryophyllaceae*, *Violaceae*, *Leguminosae*, *Boraginaceae*, *Myrtaceae*, and *Nyssaceae*, are known for their high accumulation of Co and are also recommended as biogeochemical indicators. These plants growing in soils over serpentine or Cu–Co ores may contain Co as high as 2500 to 17,700 mg/kg (AW).⁶¹³ Brooks^{104,1244} described *Hausmaniastrum* sp. as hyperaccumulators of Co, containing up to about 4000 mg/kg Co without having toxicity symptoms when grown in soil overlying a Co–Cu ore body. According to Faucon et al. (2007), two hyperaccumulators, *Acalypha* and *Hausmaniastrum* concentrate Co within the range 21–1971 mg/kg (median 426 mg/kg). On the Co-deficient coastal sands of North Carolina, leaves of *Nyssa sylvatica* (black gum) contained from 1 to 216 mg/kg Co, whereas broomsedge (*Andropogon* sp.) contained only 0.05–0.81 mg/kg.⁷⁴⁴ Foliar Co concentration in *Nyssa sylvatica* grown in Co-contaminated soil was as high as 800 mg/kg, and according to Malik et al. (2000) this plant may be used for phytoextraction of Co and ⁶⁰Co from contaminated and/or mineralized soils. These authors suggested that also *Alyssum* species offer a promise for the remediation of Co-contaminated soils.

Moss samples collected in Norway in the period 1990–1995 contained Co from 0.045 to 0.7 mg/kg, at the average value of 0.37.¹²²³

II RHODIUM

A INTRODUCTION

Data on Rh are too scarce to estimate its real environmental abundance. Some authors consider Rh as the least frequent element of the PGMs. The average content of Rh in the bulk continental crust is given as 0.06 µg/kg (Table 3.2), and its range in different rocks from 0.01 to 20 µg/kg (black shells). In coal, Rh was found at a concentration of <100 µg/kg. Pyrrhotites (iron sulfide with variable Fe content) contain Rh up to 7 mg/kg.⁸⁸⁸ Rh reveals both siderophilic and chalcophilic characters. Oxidation stages of Rh may vary, however, most commonly it occurs at the +3 valence (Table 14.1).

There are very few Rh-bearing minerals. Annual production of Rh has been roughly estimated as 25 tons (Wikipedia, January 2009). In minerals, Rh is associated with other PGMs. They are mainly arsenosulfides: hollingworthite (Rh, Pd, Pt)AsS, and irarsite (Ir, Ru, Rh, Pt)AsS. The Pt-mineral, sperrylite, can contain a large proportion of Rh and some of Fe and Cr minerals may host Rh. This metal is known to be concentrated also in siderites at the order of 0.0X–0.X mg/kg, and it may be expected to be elevated around some Fe processing industries.

The melting point of Rh is much higher than that of Pd and Pt, and this metal is also less subjected to chemical reactions than other PGMs. Rh is used mainly for the production of jewelry and of special tools, but also as a catalyst in organic synthesis, and for catalytic converters of cars.

B SOILS AND PLANTS

Data on Rh in soils are too scarce to evaluate its mean abundance in soils (Table 3.2). Eriksson (2001) reported for Swedish arable soils the content of Rh at the mean value of <40 µg/kg. Occurrence of Rh in Swedish environment is presented as follows (in µg/kg): background soil, 0.07–0.13; urban soil, 0.14–20.5; and sewage sludge, 0.26 (Ravindra et al., 2004). In soils along Austrian motorways, the mean Rh content is 13 µg/kg (Fritsche and Meisel, 2004). The Rh contents in dust samples collected in 1999 along the highways in Germany ranged from 30 to 42 µg/kg (Djingova et al., 2003). The Pt/Rh ratio in soil samples is a good indicator for the Rh source from automobile catalysts.

According to Eriksson (2001) mean concentration of Rh in cereal grains is <1 µg/kg. Plants grown along highways in Germany contained Rh, as follows (in µg/kg): dandelion, 2.2; plantain, 1.3; and moss, 5.4 (Djingova et al., 2003). Hooda et al. (2008) calculated that >50% of Rh in plants is from soils adjacent to road networks and not from aerial pollution.

III IRIDIUM

A INTRODUCTION

Mean content of Ir in the bulk continental crust is estimated at 0.05 µg/kg (Table 3.2), and in the upper continental crust as 0.02 µg/kg. It is concentrated in the Fe–Ni core and in some meteorites. Like other PGMs, Ir occurs as natural alloys, mainly with Rh and Os, in arsenosulfide minerals. Generally, Ir is considerably more often associated with Fe, Cu, and Ni sulfide deposits than are other PGMs.

Increased Ir content of sedimentary rocks, at the border layer between cretaceous and tertiary deposits, is apparently related to an effect of the meteorite collision about 5 million years ago (Dai et al.¹²⁷¹). According to Fenner and Preslay (1984) geochemical behavior of Ir is very close to that of Co and Ni. It is concentrated in some coals, up to about 200 µg/kg.

Iridium is found as uncombined element, and also as the iridium–osmium alloys osmiridium and idrosmine. Its worldwide production is estimated at around 3 tons/year (Wikipedia, January 2009).

The melting point of pure Ir is very high and its resistance to corrosion is the greatest among other PGMs. Due to a great mechanical strength at high temperatures, Ir is used for special alloys and also as a catalyst in different chemical processes. Previously Ir was commonly used for tips of ink pen. Radioactive ¹⁹²Ir is used industrially as a radiotracer in the oil industry and in gamma radiography to identify flaws in metal castings and welded joints. This isotope is also used medically to treat various types of cancer.

B SOILS AND PLANTS

Swedish arable soils contain Ir at the average value of <40 µg/kg (Eriksson, 2001). Increased levels of Ir, up to around 5 µg/kg, was reported for soil humus layer (topsoil) from the Kola Peninsula.¹⁴⁵⁷ Increased Ir levels in soils adjacent to a motorway are attributed to motor vehicles with catalysts

(Zereini et al., 1997). Contents of Ir in soils along Austrian motorways range from 0.03 to 0.89 $\mu\text{g/kg}$ and average 1.1 $\mu\text{g/kg}$ (Fritsche and Meisel, 2004). In dust collected along streets in Germany, Ir contents vary from 1.2 to 3.5 $\mu\text{g/kg}$, and in plants grown along those roads; it ranges from <0.02 to 0.4 $\mu\text{g/kg}$, being the highest in dandelion (Djingova et al., 2003).

Iridium is apparently easily taken up by plants and concentrated in leave margins. According to data presented by Bowen,⁹⁴ the Ir content of land plants is <20 $\mu\text{g/kg}$. Wheat and barley grains from Sweden contain Ir at the average value of <0.1 $\mu\text{g/kg}$ (Eriksson, 2001).

15 Elements of Group 10 (Previously Part of Group VIII)

The Group 10 contains three elements: nickel (Ni), palladium (Pd), and platinum (Pt). Ni belongs to the iron family that also includes Fe and Co, whereas Pd and Pt are noble metals of the PGMs. On the basis of the IUPAC recommendation, these elements will be described under one group. All three metals reveal variable properties (Table 15.1), siderophilic and/or lithophilic characters, and a tendency to occur under various oxidation states. All metals readily form sulfide and sulfarsenide compounds.

It should be emphasized, however, that there is other classification system excluding the elements of PGEs (i.e., Ir, Os, Pd, Pt, Rh, Ru), also called noble metals. This has a practical reason because cosmochemistry, geochemistry, and environmental relevance of all PGEs are relatively similar. Especially environmental stress due to emission of Pt, Pd, and Rh by automobile catalysts has become a real concern (Rauch and Morrison, 2008).

Some of the PGMs apparently are readily absorbed by plants when they occur in easily soluble forms in substrata.²⁴⁸ Farago and Parsons⁹⁹¹ reported that all the PGMs produce toxic symptoms in the test plant, water hyacinth. Toxicities of these metals to plants vary and decrease in the following order: $\text{Pt}^{2+} \sim \text{Pd}^{2+} > \text{Ru}^{3+} \sim \text{Ru}^{2+} \sim \text{Ir}^{3+} > \text{Os}^{4+} \sim \text{Pt}^{4+} > \text{Rh}^{3+}$.

I NICKEL

A INTRODUCTION

In the Earth's crust, the mean Ni abundance has been estimated around 20 mg/kg, whereas in the ultramafic rocks Ni ranges from 1400 to 2000 mg/kg (Tables 3.2 and 15.2). Its concentrations decrease with increasing acidity of rocks, down to the range of 5–20 mg/kg in granites. Sedimentary rocks contain Ni in the range from 5 to 90 mg/kg, with the highest range being for argillaceous sediments.

Nickel reveals both chalcophilic and siderophilic affinity and readily combines with metallic Fe. Therefore, Ni–Fe compounds are common in the Earth's core and meteorites. The Ni–Fe alloy of the Earth's core (called barysphere or NIFE) is composed of Fe/Ni within the ratio of 11:1 (Fairbridge, 1972). The great affinity of Ni for S accounts for its frequent association with segregates of S bodies. The principal Ni metallic ores are composed mainly of pentlandite, $(\text{Ni,Fe})_9\text{S}_8$ and pyrrhotite (iron sulfide with variable Fe content; Fe_{1-x}Ni). In rocks, Ni occurs primarily as sulfides (millerite, NiS), arsenides (niccolite, NiAs), and antimonides (ullmanite, NiSbS). Ni often forms sulfides and sulfarsenides together with Fe and Co, and is associated with several Fe minerals.

After weathering, most Ni is coprecipitated with Fe and Mn oxides, and becomes included in goethite, limonite, serpentinite, as well as in other Fe minerals. It is also associated with carbonates, phosphates, and silicates. During weathering of Ni-rich rocks (mainly in tropical climates), the formation of garnierite, $(\text{Ni, Mg}) \text{SiO}_3 \cdot n\text{H}_2\text{O}$, which is a poorly defined mixture of clay minerals, is observed. OM exhibits a strong ability to absorb Ni, thus it is likely to be highly concentrated in coal and oil. This concentration is apparently also an effect of the precipitation of Ni as sulfides in sediments rich in organisms and under reducing conditions. Therefore, a significant proportion of Ni loads to the environment is from biolite combustion. Global emission of Ni from coal combustion is

TABLE 15.1
Selected Properties of Trace Elements of Group 10

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C, g/cm ³)	Valence ^b
Ni, nickel	28	58.69	162	8.90	+ 2 , +1, +3, +4
Pd, palladium	46	106.42	178	12.02	+ 2 , +1, +3, +4
Pt, platinum	78	195.07	183	21.45	+ 4 , +2, +3, +5

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation states.

calculated to be around 20 kt/yr, and from oil products combustion it is estimated to range from 10 to >40 kt/yr.¹³⁵⁷

Global Ni production was estimated to be 1.614 Mt in 2008 (USDI, 2009). Its anthropogenic cycle is broadly described by Reck et al. (2008), who estimated that 68% of this metal is used for stainless steels. It is also widely used for magnetic components and electrical equipments. Ni-alloys are used for different tools and vessels used in medicine and in food technology, as well as for kitchen equipment (e.g., cutlery). Its compounds are utilized as dyes in ceramic and glass manufactures, and in batteries containing Ni–Cd compounds.

B SOILS

The Ni status of soils is highly dependent on its contents in parent material. However, the concentration of Ni in surface soils reflects the additional impact of both soil-forming processes and anthropogenic activities. Ni is quite abundant in all soil groups and its greater accumulation is observed in Cambisols and Calcisols (Table 15.2).

Soils throughout the world contain Ni in the very broad range, however its mean concentrations, as reported for various countries are within the range 13–37 mg/kg (Table 3.2). The highest Ni

TABLE 15.2
Abundance of Ni in Rocks and Soils (mg/kg)

Rock/Soil	Ni
Earth's crust	20
Igneous rocks	—
Ultramafic	1400–2000
Mafic	130–160
Acid	5–20
Sedimentary rocks	—
Argillaceous	40–90
Sandstones	5–20
Calcareous	5–20
Soils ^a	29
Arenosols (sandy)	7–33
Podzols (medium loamy)	11–25
Cambisols (heavy loamy)	23–50
Calcisols (calcareous)	18–92
Histosols (organic)	4–12

^a Soil groups are given according to the WBR (Table 3.1).

contents are given for uncontaminated soils of various countries, as follows (in mg/kg): (1) 119, Canada;²⁴³ (2) 450, China;¹¹²⁴ (3) 660, Japan;⁶⁶⁰ and (4) 3240, Italy.⁹⁴⁶ Soils of South Africa contain Ni within the range of 3.43–159 mg/kg, and the maximum permissible level in agricultural soils, established in 1997, is 50 mg/kg (Herselman et al., 2005). The baseline levels for Ni in soils of Brazil is given (in mg/kg) as 0.5 for sandstone soil and 11.5 for limestone soil (Melo et al., 2006).

The Ni distribution in soil profiles is related either to OM or to amorphous oxides and clay fractions, depending on soil types. Usually a close relationship between Ni in soils and CEC, and clay content is observed (Senwo and Tazisong, 2004). The lowest Ni level (7.6 mg/kg) was in soil with 0.9% clay content, and the highest (53.8 mg/kg) in soil with 4.6% clay content. Bettinelli et al. (2000) reported Ni contents at 27 and 88 mg/kg in light sandy soil and calcareous loam, respectively. Soils of the taiga zone of Western Siberia contain Ni within the range of 20–100 mg/kg (Niechayeva, 2002). In surface horizons of Russian chernozems, mean Ni contents range from 28 to 34 mg/kg (Protasova and Kopayeva¹¹²³). Geometric mean Ni content in soil from major agricultural production areas of the United States is 16.5 mg/kg, ranging from 0.7 to 269 mg/kg.¹³²⁹ The median Ni content of sandy soils of Lithuania is 9 mg/kg, and of loamy clayed soils is 17 mg/kg.¹³⁵⁹ The total content of Ni in soils of Finland is 60 mg/kg at the 90th percentile.¹³⁶⁸ Ni levels are elevated in some organic-rich soils. Especially peaty serpentine soils are known for high Ni levels (Table 15.3), existing in easily soluble organic complexes.⁵⁶⁶ Also, soils of arid and semiarid regions are likely to have a high Ni content. Roca et al. (2008) observed, in Argentina, the relationship between WRB soil groups and Ni content, being the lowest in calcisols (10.6 mg/kg) and the highest in fluvisols (21.01 mg/kg). Contents of Ni in soils of Barcelona Province, Spain, range from 2.3 to 186 mg/kg, showing the positive correlation with the clay and silt fractions (Bech et al., 2008).

Nickel is easily mobilized during weathering, and unlike Mn^{2+} and Fe^{2+} , Ni^{2+} is relatively stable in aqueous solutions and is capable of migration within soil profiles. Fe oxides and minerals contain Ni within the range from 100 to 170 mg/kg, whereas Fe–Mn concretions accumulate this metal up to 680 mg/kg. Mn oxides in soils accumulate Ni in the range from 39 to 4900 mg/kg, and Mn minerals present in sediments contain this metal from 120 to 10,900 mg/kg (Table 4.3). However, less than 15 to 30% of the total Ni is extracted with the Mn oxides.⁵⁷⁰ Norrish⁵⁷⁰ stated that the fraction of soil Ni carried in the oxides of Fe and Mn seems to be the form easily available to plants. Ni sorption on Fe and Mn oxides is especially pH dependent, probably because NiOH^+ is preferentially sorbed and also because the surface charge on sorbents is affected by pH.⁹⁴⁸ Also clay minerals,

TABLE 15.3
Nickel Enrichment and Contamination in Soils (mg/kg)

Site and Pollution Source	Mean or Range in Content	Country	Reference
Soil over serpentine rocks	770	Australia	702
	1700–5000	New Zealand	495
	3563–7375	Rhodesia	566
Mine wastes	2–1150	Great Britain	289
Metal-processing industry	206–26,000	Canada	150, 245, 775
	500–600 ^a	Great Britain	38
	304–9288	Russia	1217
	26–36 ^b	Sweden	811
Sludged farmland	23–846	Great Britain	59, 959, 987
	31–101	Holland	314
	50–84	Germany	176

^a Soluble in HCl.

^b Needle litter and humus layer, respectively.

in particular montmorillonite, exhibit a great capability to bind this metal (Dähn et al., 2003). Generally, the mobility of Ni is inversely related to the soil pH. This is clearly demonstrated by Siebielec and Chaney (2006), who reported a drastic decrease of the Ni extractability at soil pH above 6.5. Ni retention in noncalcareous soils with pH 3.6–6.7 results in the displacement of Ca, Mg, and Na into soil solution that affected in decrease in soil solution pH (Ponizovsky et al., 2008b).

Nickel in soils is slightly mobile and occurs mainly in the residual fraction, in more than 50% of its total contents in loamy sandy soil, and in about 70% of its occurrence in estuary muck (Zhang et al., 2004). However, in surface soil horizons, Ni occurs mainly in bound organic forms, a part of which are relatively easily soluble chelates. Bonding of Ni to organic ligands may be very strong, and can highly affect its mobility. Conversely, the remobilization of Ni from solid phases appears to be possible in the presence of FA and HA. Thus, Ni may be quite mobile in soils with high complexation ability (e.g., organic-rich and polluted soils). There also is observed a high adsorption capacity of HA and FA for Ni in cotton compost and poultry manure (Tejada et al., 2008). The important and complex role of HA and FA in binding Ni species may be described by the WHAM VI model used for the prediction of metal partitioning in soil suspension (Tipping, 1998).

Forms of Ni in soils are diverse and range from highly mobile to ones that have no reactivity. Several soil properties, particularly clay fraction, SOM, and pH, control Ni behavior, and phytoavailability, in particular. Massoura et al. (2005a) reported that Ni associated with phyllosilicates is more easily taken up by plants than that associated with Fe oxides. Isotopic exchange kinetics, based on the soil-solution distribution coefficient of the radionuclide, ^{63}Ni , is proposed as an easy method to measure the available fraction of Ni in soils (Echevaria et al.,¹²⁸⁶ Massoura et al., 2005b).

The transformation of mobile Ni fractions (exchangeable, carbonate-bound, Fe–Mn oxide-bound, and OM-bound) to residual fraction is observed during aerobic composting of sewage sludge (Zheng et al., 2007). Rajaie et al. (2008) reported that Ni sulfate added to calcareous soils was transformed into oxides and, to a lesser extent, into residual fraction what affected its lower bioavailability. According to Tejada et al. (2008), in soil amendment with organic wastes, Ni became adsorbed by HA and FA and thus less toxic to microbiota. On the other hand, Bloomfield⁸¹ stated that although OM is able to mobilize Ni from carbonate and oxide fractions as well as to decrease its sorption on clays, the bonding of this metal to the organic ligands could not be particularly strong. Complexing ligands, such as SO_4^{2-} and organic acids, reduce the sorption of Ni. Thus, Ni may be quite mobile in soils with high complexation ability (e.g., organic-rich and polluted soils).

Changes in mobility and retention of Ni in various soils were a subject of several studies (Evecharria et al., 1998; Stauton et al., 2002). Ni added to soil (e.g., Ni-spiked soil) became, with time, immobile that resulted in a large decrease in Ni concentrations in soil solution, especially in calcareous soils (Ponizovsky et al., 2008a).

Concentrations of Ni in natural solutions of surface horizons of different soils vary from 3 to 150 $\mu\text{g/L}$, depending on soil types and techniques used for obtaining solution.^{311,892}

Information on Ni ionic species in the soil solution is rather limited, but the Ni species described by Garrels and Christ²⁵⁶ such as Ni^{2+} , NiOH^+ , HNiO_2^- , $\text{Ni}(\text{OH})_3^-$ are likely to occur when Ni is not completely chelated. Also complex compounds like $\text{Ni}(\text{OH})_2^0$ and NiSO_4^0 , of a relatively high stability constant, are known to occur in soil solution (Kabata-Pendias and Sadurski, 2004).

1 Soil Contamination

Nickel is considered as a serious pollutant that is released from metal processing plants and from the increased combustion of coal and oil. Also some sewage sludges and phosphate fertilizers may be importance sources of Ni in agricultural soils. The Ni balance in soils of crop farms varies significantly (in g/ha/year) from -3.3 in Denmark to 33 in France (Eckel et al., 2005). The highest contamination by Ni, up to 26,000 mg Ni/kg , was reported for topsoils near the Ni–Cu smelter at Sudbury, Canada (Table 15.3). Emission from the Ni industry of Russia has affected elevated levels of Ni in soils of Norway. The concentrations of HNO_3 -extractable Ni varied in surface agricultural soils of this region from 6.25 to 136.88 mg/kg (mean 30.43), whereas the background content was

estimated as 25 mg/kg (Almås et al., 1995). In Albania, soils around the Burrel chromium smelter contain Ni up to 1243 mg/kg (Shtiza et al., 2005).

In the distance within 4 km from the Norilsk Nickel Company (Russia) the absence of trees and the disturbance of OM mineralization processes is observed, mainly due to Ni contamination (Yakovlev et al., 2008). Elevated Ni content in soil is reported to decrease the activity of some enzymes, such as dehydrogenase, urease, and acid and alkaline phosphatases (Wyszkowska et al., 2008).

Some municipal sludges are enriched in Ni, and for American cities its content is reported to range between 29 and 800 mg/kg, with a median value of 195 mg/kg (ATSDR, 2002). Application of sludge to soil usually increases the Ni mobility, mainly due to complexation with dissolved organic compounds.

Phytoremediation of Ni-contaminated soils is broadly studied by some authors (Chaney et al., 2005; Doherty et al., 2008; Panwar et al., 2002; Terry and Banuelos, 2000).

C PLANTS

1 Absorption and Biochemical Functions

There is no evidence of an essential role of Ni in plant metabolism, although several investigators suggested that Ni might be essential for plants.^{531,542} The essentiality of Ni for some biosynthesis of a number of bacteria has been proven. Also its role in the nodulation of legumes and effects on the nitrification and mineralization of some OM was described.⁹⁷⁸ Thus, Ni is considered as essential for legumes in which is involved in the urease metabolism (Eskew et al., 1983). Welch⁸⁵⁹ discussed reports that Ni is an essential component of the enzyme urease, and thus Ni may be required by nodulated legumes that transport N from roots to tops in forms of ureide compounds. Dalton et al.⁹⁷⁵ reported that microorganisms that metabolize H₂ and urea are highly sensitive to Ni supply.

Studies of the uptake and chemical behavior of Ni in plants are related mainly to its toxicity having possible implications with respect to animals and human. Restricted growths of plants and injuries caused by an excess of Ni were observed for quite a long time.

The mechanism of Ni toxicity and biological effects are highly related to its species. The cationic form, Ni²⁺, is more readily absorbed and more toxic than its complexed forms. Molas¹⁴²² observed that Ni-glucose chelate was more toxic to cabbage than Ni-EDTA complex, and described various morphological and anatomical changes caused by an *in vitro* excess of Ni.

The Ni content of plants seems to be highly controlled by soil properties and origin, however, plant abilities to absorb Ni (e.g., accumulators and hyperaccumulators) also has a strong influence. Staunton et al.¹⁵⁰⁴ noted that the secretion of organic anions, and modification of soil pH by roots and fungi in the rhizosphere may decrease Ni adsorption by soils components, and thus increase its plant availability. The easy phytoavailability of Ni to plants is demonstrated by the results of an experiment with ⁶³Ni, where the isotopic composition of soil solution was the same as in plants, during the same time.¹²⁸⁶ Cataldo et al.¹²⁴ studied distribution, and forms of Ni in soybean plants and observed that when Ni is in the soluble phase, it is readily absorbed by roots. Ni uptake by plants is positively correlated with Ni concentrations in solutions, and the uptake mechanism is multiphasic (Figure 15.1). A strain of *Pseudomonas* was investigated by Bordons and Jofre⁹⁵⁰ for its Ni accumulation capacity. Results indicated an extracellular, metabolically independent adsorption, and a possible displacement by Ni²⁺ of Mg⁺ from the membrane. All Ni²⁺ retained by bacteria was accumulated externally to cells.

Nickel is usually easily extracted from soils by plants and its contents of plants are simple functions of Ni forms in soils (Figure 15.2). Both plant and pedological factors affect these processes and the most pronounced factor is soil pH. Berrow and Burridge⁶⁸ found that increasing soil pH from 4.5 to 6.5 decreased the Ni content of oats by a factor of about 8.

Like other divalent cations (e.g., Co²⁺, Cu²⁺, and Zn²⁺), Ni²⁺ is known to form organic compounds and complexes. Tiffin⁷⁸⁹ found Ni bound to anionic organic complexes in xylem exudates. The Ni transport and storage seems to be metabolically controlled, it is mobile in plants and is likely to be

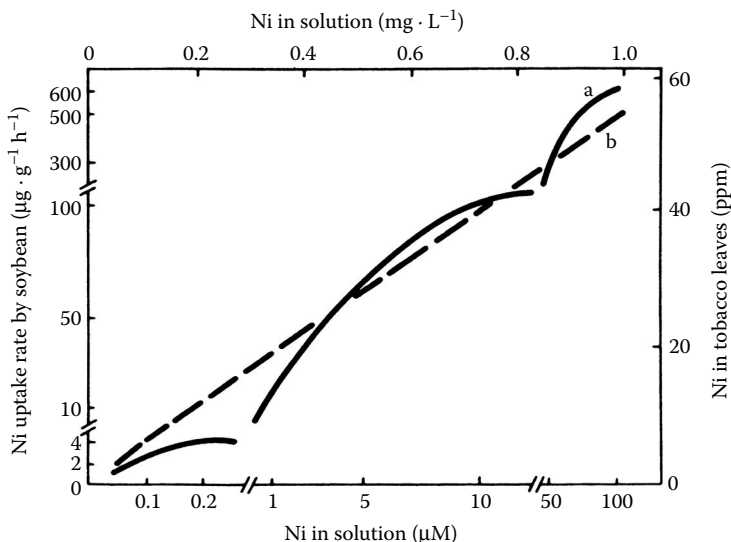


FIGURE 15.1 Effects of Ni concentration in solution on Ni uptake by plants. (a) Molar Ni concentrations on the rate of Ni uptake 21-day-old intact soybeans (whole plant); (b) Ni concentration in solution on Ni content of tobacco leaves. (Data compiled from Cataldo, D. A., Garland, T. R., and Wildung, R. E., *Plant Physiol.*, 62, I, 563; II, 566, 1978; Welch, R. M. and Cary, E. E., *J. Agric. Food Chem.*, 23, 479, 1975.)

accumulated in both leaves and seeds.^{176,301,860} The metal origin also plays a significant role in its availability to plants. Grupe and Kuntze¹⁰¹⁸ reported a much higher Ni uptake by cereals from the soil with added metal than from its lithogenic source, what suggests that Ni solubility is a key factor influencing its toxicity to plants. Rooney et al. (2007) suggested that CEC value of soils is the best predictor for the Ni toxicity.

The mechanism of Ni toxicity to plants is not fully understood, although the restricted growth of plants and injuries caused by an excess of this metal was observed for quite a long time. Biological effects of Ni are highly related to its species. However, Ni speciation in the plant extract indicated that regardless of chemical forms added to the soils, Ni was only found in neutral and negative complexes.¹⁵⁴³ According to Molas¹⁴²² Ni fixed with glutamic acid was the most toxic to cabbage, and the least toxic was the Ni-EDTA complex. The most common symptom of Ni phytotoxicity is chlorosis, which seems to be Fe-induced chlorosis. Indeed, Foy et al.²⁴¹ reported a low foliar Fe level at toxic concentrations of Ni in the growth medium. In plants under Ni stress, the absorption of nutrients, root development, and metabolism are strongly retarded. Before the acute Ni toxicity symptoms are evident, elevated concentrations of this metal in plant tissues are known to inhibit photosynthesis and transpiration.⁵⁶ Also, low N₂ fixation by soybean plants was reported to be caused by Ni excesses.⁸²⁴ Thakali et al. (2006) adapted the TBLM for the assessment of Ni toxicity and concluded that metal ions react with the biotic ligand and the receptor site and inhibit barley root elongation. These authors concluded that the TBLM may be used to predict EC₅₀ Ni concentration to assess its risk in soils. Gajewska and Skłodowska (2008) described that elevated Ni concentration in nutrient solution decreases the activity of superoxide dismutase and catalase of wheat shoots, while increases the activity of peroxidases and glutathione S-transferase. Addition of Ni, at concentration 200 mg/kg to two soils, heavy loamy sand and light silty loam decreased oat yield by 65% and 40%, respectively (Wyszkowska et al., 2007).

Under natural conditions, Ni toxicities are associated with serpentine or other Ni-rich soils. Some native plants from such locations accumulate leaf concentrations of over 6000 mg Ni/kg. Mesjarz-Przybyłowicz et al. (2004) reported the Ni concentration at 18,000 mg/kg in *Berkheya coddii*, an endemic plant growing on Ni-enriched ultramafic soils (South Africa) containing 1300 mg Ni/kg.

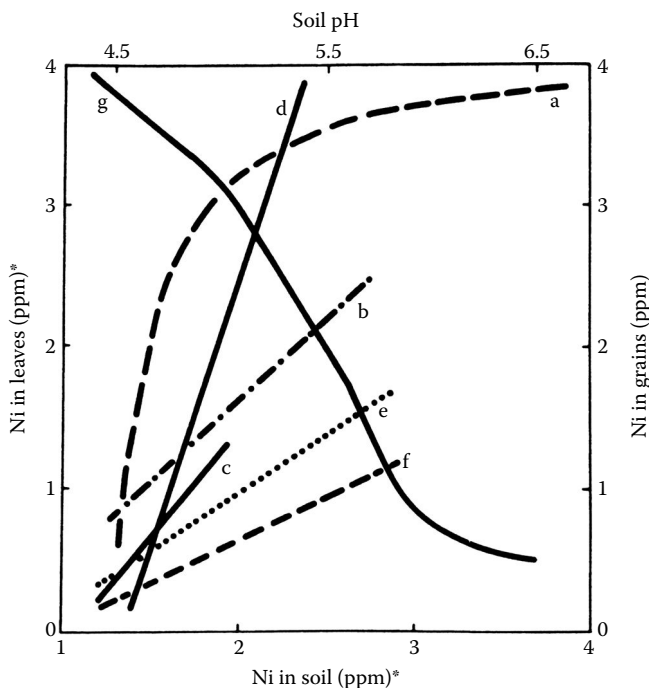


FIGURE 15.2 Ni concentrations in plants as a function of Ni content of soils. (a) Leaves of *Alyssum* sp., accumulating Ni; (b) leaves of *A. montanum*, nonaccumulating Ni; (c) wheat leaves; (d) barley grains; (e) carrot roots; (f) radish roots. The influence of soil pH on Ni concentration in (g) oat grains. *Ni concentrations in soils, leaves, and roots are given in powers of ten. (Data compiled from Berrow, M. L. and Burridge, J. C., *Proc. Int. Conf. on Management and Control of Heavy Metals in the Environment*, CEP Consultants Ltd., Edinburgh, U.K., 304, 1979; Diez, Th. and Rosopulo, A., *Sonderdruck Landw. Forsch.*, 33, 236, 1976; Morrison, R. S., Brooks, R. R., and Reeves, R. D., *Plant Sci. Lett.*, 17, 451, 1980; Pilegaard, K., *Bot. Tidsskr.*, 73, 167, 1978.)

Anderson et al.²³ reported that oats, a Ni-sensitive crop, when affected by this metal, contained Ni in leaves within the range of 24–308 mg/kg. The phytotoxic Ni concentrations range widely among plant species and cultivars and are reported for various plants to be from 40 to 246 mg/kg.²⁷⁹ Davis et al.¹⁷¹ found the toxic Ni content of barley seedlings to be as low as 26 mg/kg, whereas Khalid and Tinsley³⁸⁹ found 50 mg/kg Ni in ryegrass to cause slight chlorosis. Growth and survival of hybrid poplars show severe phytotoxicity above 1 mg Ni/L in the growth media.¹⁴⁶⁴ Generally, the range of excessive or toxic amounts of Ni in most plant species varies from 10 to 100 mg/kg (Table 5.4). Most sensitive species are affected by much lower Ni concentrations, ranging from 10 to 30 mg/kg.^{1052,1081} Chang et al. (1992) attempted to establish the phytotoxicity threshold for Ni and determined that the PT_{50} leaf tissue corresponds to 3 mg Ni/kg and is much lower than Ni concentrations reported to be associated with its phytotoxicity levels. These authors suggested that the typical plant tissue Ni concentration is approximately 10 mg/kg. Generally, the range of excessive or toxic amounts of Ni in most plant species varies from 10 to 1000 mg/kg. Increased level of Ni in nutrient solution (40 mg/L) affected decreased growth, photosynthesis, and cation (Na, K, Ca) absorption by mungbean cultivars (Ahmad et al., 2007).

Several plant species are known for their great tolerance and hyperaccumulation of Ni. Usually these species, mainly of the *Boraginaceae*, *Cruciferae*, *Myrtaceae*, *Leguminosae*, and *Caryophyllaceae* families, are also Co accumulators. Native vegetation of serpentine soils was reported to contain up to 19,000 mg/kg (AW) Ni.⁴⁹⁴ *Hybanthus floribundus* (*Violaceae* family) growing on acid ferralsols accumulated 6542 mg/kg Ni in leaves, 5490 mg/kg in stems, and 221 mg/kg in root

TABLE 15.4
Nickel in Food Plants Grown in Various Countries^a (mg/kg)

Plant	Range	Mean
Wheat, grains	0.17–0.67	0.34
Barley, grains	0.10–0.67	0.41
Oats, grains	0.20–8.0	1.28
Peas and beans, seeds	0.2–0.25	—
Cabbage, leaves	0.6–3.3	1.03
Carrot, roots	0.26–0.98	—
Onion, bulbs	0.59–0.4	—
Tomato, fruits	0.43–0.48	—
Cucumber, fruits	1.3–2.0	—
Potato, tubers	0.29–1.0	—
Apple, fruits	—	0.06
Orange, fruits	—	0.39
Hazelnuts and walnuts	1.6–1.7	—
Cocoa, powder	5–10	—

^a Presented are common, possible background, values from various sources.

bark.⁷⁰² The pronounced ability of some plant species to accumulate Ni when grown in soil over Ni ore bodies may make them useful biogeochemical indicators.^{417,553,899}

There is a great number of plants, 317 taxa of 37 families, which have the ability to accumulate over 1000 mg Ni/kg (Greger, 1999). The most common Ni accumulators are *Alyssum* sps., and Chaney was one of the first to suggest the possible phytoextraction of Ni from polluted soils, using these species that can accumulate over 400 kg Ni from one hectare (Chaney et al., 1999). Bani et al. (2007) reported that 25 kg Ni/ha may be phytoextracted by *Alyssum murale* from the fertilized plots. The mechanism of the Ni hyperaccumulation is not yet well-understood, but evidently it is associated with organo-metallic complexes. An association has been found between Ni concentration in the sap of several genotypes of hyperaccumulators and concentrations of some organic acids (polycarboxylate), especially of citric acid.¹²⁴⁴ Apparently these complexes react as transport-ligands for Ni within plants which have accumulated the metal. According to Asemaneh et al. (2006), the main ligands for Ni in hyperaccumulators are citrate and malate, involved in the metal transfer within plant tissues. Ni is likely to be concentrated in cells of leaf epidermis. However, in most plants Ni is accumulated mainly in roots. Someya et al. (2007) examined the role of rhizobacterium in the alleviation of Ni toxicity to plants and concluded that it is not associated with siderophore production. Mirete et al. (2007) identified the Ni resistance genes from the rhizosphere metagenome of plants adapted to acid mine drainage. Pohlmeier (1999) broadly reviewed mechanisms of the complexation of Ni²⁺ in plants and listed several organic ligands involved in these processes. Krämer et al.¹³⁷⁷ reported that exposing a species of *Alyssum* to Ni elicits a large increase in the levels of free histidine in an Ni-accumulator phenotype. The authors concluded that an enhanced production of histidine is responsible for the Ni hyperaccumulation in these plants. Nicks and Chambers¹⁴⁴¹ have described a great variation in Ni content (3280–7820 mg/kg) of individual plants of one species of the *Brassicaceae* family that is endemic to serpentine soils in California.

The easy phytoavailability of Ni is of a real environmental concern. Increased Ni levels in food plants are associated with health hazards. The ready transfer of Ni from soils to vegetables has been illustrated by Frank et al. (1982) in the notable accumulation of this metal, up to 4000 mg/kg, in cabbage heads and celery roots and tops planted on soil around a Ni smelter (Niagara Peninsula), with Ni contents between 500 and 1500 mg/kg.

2 Interactions with Other Elements

The interaction between Ni and other trace metals, Fe in particular, is believed to be a common mechanism involved in the Ni toxicity. Cataldo et al.¹²⁴ found that the absorption of Ni by soybean roots and Ni²⁺ translocation from roots to shoots were inhibited by the presence of Cu²⁺, Zn²⁺, and Fe²⁺, whereas Wallace et al.⁸⁴⁴ stated that Fe³⁺ (as FeEDDHA) did not depress Ni concentrations in leaves of bush beans. Nevertheless, Ni excess is believed to cause an actual Fe deficiency by inhibiting the translocation of Fe from roots to tops. Khalid and Tinsley³⁸⁹ concluded that the Ni:Fe ratio, rather than the Ni and Fe concentrations in plants, shows a better relationship with the toxic effects of Ni. Both antagonistic and synergistic interactions are observed between Ni and several trace metals (Figure 5.8). Ni interactions with other trace metals affected variable reactions of soil bacteria on metal contamination, especially significant changes were observed for Ni–Cd, Ni–Pb, and Ni–Cr (Wyszkowska et al., 2007).

3 Concentrations in Plants

The Ni contents of plants growing on uncontaminated soils may vary considerably because it is reflecting both environmental and biological factors. However, its concentrations in certain food plants from different countries do not differ widely.

In food plants, Ni content varies from 0.06 to 2 mg/kg with the lowest value in apples and the highest in cucumber (Table 15.4). Average Ni contents of cereal grains from different countries vary from 0.34 to 1.28 mg/kg and is the highest in oat grains. Barley and wheat grains from Sweden contain Ni at mean values of 0.15 and 0.16 mg/kg, respectively (Eriksson, 2001). The mean Ni contents of clover from various countries range from 1.2 to 2.7 mg/kg, whereas these values for grass are between 0.13 and 1.7 mg/kg (Table 15.5). A much higher Ni content has been reported for meadow grass (13–75 mg/kg) and forest grass (10–100 mg/kg) from taiga zone of Western Siberia (Niechayeva, 2002).

Environmental Ni pollution greatly influences its contents in plants (Table 15.6). In ecosystems where Ni is an airborne pollutant, the tops of plants are likely to concentrate the most Ni, which can

TABLE 15.5
Mean Levels and Ranges of Ni in Grass and Clover at the Immature Growth Stage from Different Countries (mg/kg)

Country	Grasses		Clovers		Reference
	Range	Mean	Range	Mean	
Belgium	0.9–1.3	1.1	—	—	684
Great Britain	0.84–2.4 ^a	—	1.3–6.2 ^a	—	67
Germany	1.3–2.5	1.7	1.0–1.3 ^b	1.2	769
Finland	0.15–1.08	0.4	—	—	590
Hungary	—	—	1.4–2.4 ^b	1.9	769
Ireland	0.8–2.2	1.4	—	2.7	235
Poland	0.3–4.7	1.7	0.2–8.2	2.5	684, 381, 1045
U.S.	<0.07–0.67	0.13	<0.5–5	1.5 ^c	200, 710
Lithuania	2.4–4.8 ^d	—	—	2.6 ^e	502

^a For freely and poorly drained soils, respectively.

^b For meadow and red clover, respectively.

^c Calculated from AW basis for alfalfa.

^d For meadow hay and grass crop, respectively.

^e Clover-timothy hay.

TABLE 15.6
Nickel Content of Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Part	Mean or Range of Content	Country	Reference
Metal-processing industry	Blueberry	4.8–6.2	Sweden	811
	Blueberry, leaves	92	Canada	866
	Celery, stalks	29	Canada	775
	Horsetail, tops	140	Canada	745
	Lettuce, leaves	2.7	Australia	57
	Lettuce, leaves	84	Canada	775
	Lettuce, leaves	11	Germany	431
	Grass	3.9–9.0 ^a	Germany	769
	Oats, grain	1.5	Germany	431
	Cereal, leaves	230–250	Great Britain	38
	Grass, tops	1700–32,000	Great Britain	38
	Onion, bulbs	47	Canada	775
	Spruce, twigs	6–14 ^b	Sweden	811
Oil refinery	Clover, tops	2.8–14.8	Poland	605
	Grass, tops	2.4–13.3	Poland	605
Sludged soils or urban gardens	Grass, tops	15–19 ^c	Holland	297
	Collard, leaves	0.1–11.6	U.S.	127
	Parsley, leaves	3.7	Poland	1015a
	Lettuce	1.8–5.8 ^d	Australia	831
	Lettuce	2.4–40.3 ^e	Great Britain	170
	Grass	10–24	Great Britain	68
	Cereal, straw	9.7–20.8	Germany	176
	Cereal, grain	1.6–5.2	Germany	176
	Soybean, seeds	7–26	U.S.	10
	Rice, leaves	11–20	Japan	395
Other sources	Oats, grain	60	Canada	301
	Alfalfa	44 ^e	Canada	301
	Sagebrush	30 ^f	U.S.	278

^a Industrial emission and urban waste waters.

^b Five- and one-year old, respectively.

^c Unwashed and washed leaves, respectively.

^d For field and greenhouse experiments, respectively.

^e Pot experiment.

^f AW basis.

be washed from the leaf surfaces quite easily.³⁸ Sewage sludge has also been shown to be a serious source of Ni as a pollutant in plants.

II PALLADIUM

A INTRODUCTION

The average abundance of Pd in the Earth's crust is estimated as 4 µg/kg (Table 3.2), but higher contents, up to 10 µg/kg, are also given (Reimann and de Caritat, 1998). It may be concentrated in ultramafic rocks, some coals, black shales, and phosphorites. Higher concentrations are found in basalts, shale schists, and some phosphorites. The arithmetic mean of Pd in the United States coal

is $<1 \mu\text{g/kg}$ (Finkelman, 1999). Mn ores and concretions are known for their capacity to accumulate Pd, which ranges from 3.7 to $11.4 \mu\text{g/kg}$. Pd exhibits relatively strong chalcophilic character and variable oxidation states (Table 15.1). In general, Pd is considered as a greater potent threat to the environment than the other PGEs. Pd is more reactive chemically and therefore occurs in more mineral forms than other PGEs. Among better-known minerals are: arsenopalladinite, Pd_3As ; stibiopalladinite, Pd_3Sb ; and potarite, PdHg . Also relatively common are sulfide minerals, like braggite (Pt,Pd,NiS) and cooperite (Pt,PdS). This metal is relatively common in several sulfide minerals (e.g., Cu and Ni sulfides), at the approximate concentration range from 0.7 to 10 mg/kg , and may be associated with ilmenite, zircon, and chromite.

The global production of Pd, in the period 1999–2002, varied from 140 to 230 t/year (Hoppstock and Sures, 2004). Estimation of the Pd production in 2008 is 206 t (USDI, 2009). This metal is widely used for electronics and jewelry production and in dentistry. Alloys with Pd are also used for bearings and springs in watches, as well as for chemical and medical instruments. Its compounds are used in photography, electroplatings, and as a catalyst, mainly in organic synthesis.

Above 50% of the Pd supply was used in the year 2000 for automotive catalytic converters. Since 1990, Pd has been added instead of Pt to some VECs, which has resulted in increased amounts of Pd released to roadside areas (Helmers and Krümmerer, 1999). The use of Pd in car converters has increased 200-fold between 1989 and 1997 (Stilianakis, 2005). Gaita and Al-Bazi (1995) calculated that 62 t of Pd are annually released in VECs. Pd, as other PGEs (Pt and Rh), used to reduce hydrocarbon, carbon monoxide, and nitrous oxide in automotive emissions poses a potential risk to the environment and human (Zereini and Alt, 2006).

Ravindra et al. (2004) broadly described uses and emission of Pd by VECs. The results of the experiment conducted by Colombo et al. (2008) indicated that Pd (and also Pt and Rh) is likely to form complexes with some inorganic ions (Cl, N, S) that contribute to its mobility in environmental and biological systems.

B SOILS

There are observed recently increased data on Pd in soils, especially along roads. Mean Pd contents in soils, as reported by different authors, range from about 1 to $40 \mu\text{g/kg}$ and average $20 \mu\text{g/kg}$ (Table 3.2). An association of Pd concentrations with clay fraction and SOM is often observed. Pd-hydroxides and complex compounds are relatively mobile in soil.

Ravindra et al. (2004) presented the broad review on Pd in roadside soils and dust. Pd concentrations vary from 6.6 to $280 \mu\text{g/kg}$, being higher in dust. Swedish arable soils contain Pd in the range of <40 – $150 \mu\text{g/kg}$, at an average value of $40 \mu\text{g/kg}$ (Eriksson, 2001). Also in the Report of the UNEP/WHO (2002), its mean content is given as $40 \mu\text{g/kg}$.

The VECs used recently for vehicles become a significant source of Pd, and as Hooda et al. (2008) stated, soil Pd at the road perimeter is higher than Pt or Rh, apparently due to difference in its use. Soils near German highway contain Pd in the range between 1 and $47 \mu\text{g/kg}$, at an average value of $6.6 \mu\text{g/kg}$ (Zereini et al., 1997; Ravindra et al., 2004). According to Wichman et al. (2007), maximum Pd concentration in soils along heavy traffic roads in Germany is $43.3 \mu\text{g/kg}$. Zereini et al. (2007) reported that increased level of Pd in meadow soils was detected as far as 50 m from the highway. Soils along Austrian motorways contain Pd up to $25 \mu\text{g/kg}$ (Fritsche and Meisel, 2004) and soils from Mexico City— $70 \mu\text{g/kg}$ (Morton et al., 2001). Roadside soils from Sao Paulo contain Pd within the range 1.1– $58 \mu\text{g/kg}$ (Morcelli et al., 2005). Concentration of Pd in sediments of residential streets in Hawaii reached $105 \mu\text{g/kg}$ (Sutherland et al., 2007). Contents of Pd in soils from the Napoli metropolitan area vary from 8 to $110 \mu\text{g/kg}$, with a mean value of $12.7 \mu\text{g/kg}$ and indicate a positive relationship with the traffic density, whereas in the urban areas of Campania region its contents vary from <0.5 to $4327 \mu\text{g/kg}$ (Cicchella et al., 2003, 2008). In Athens, Pd in soils along highways averaged $125.9 \mu\text{g/kg}$, while in the urban street was 38% lower (Riga-Karandinoas et al., 2006). Concentrations of Pd in roadside dust range from 1 to $26 \mu\text{g/kg}$ near Frankfurt and from 20

to 115 µg/kg near San Diego, California (UNEP/WHO, 2002). High Pd contents are reported for road tunnel dust, from 20 to 297 µg/kg (Helmers et al., 1998). Results presented by Ljubomirova et al. (2008) show that up to 70% of Pd in street dust is in mobile forms.

The Ni industry on the Kola Peninsula is a source of Pd in soils. Its increased level in 0-horizon of soils is observed within the distance up to about 200 km (Niskavaara et al., 2004).

C PLANTS

Palladium seems to be easily available to plants when it occurs in mobile forms. The accumulation of Pd by plants takes place in both experimental and natural conditions. Its contents in various shrubs and trees are in the range of 30–400 µg/kg AW. In twigs of birch grown close to the mineral deposits of PGEs in Canada, Pd is accumulated up to 4014 µg/kg (UNEP/WHO, 2002). Barley and wheat grains from Sweden contain Pd at a mean value of <1 µg/kg (Eriksson, 2001). Its contents in staple foods vary from <0.1 to 3 µg/kg FW, being the highest in nuts (Table 15.7).

Plants exposed to automobile exhausts contain Pd in the range from 0.43 to 2.4 µg/kg, with the highest value for moss and the lowest for plantain (Djingova et al., 2003). Pd concentration in mosses decreased with increasing distance from the road and reach background values at the distance between 10 and 200 m (Zechmaister et al., 2006). Grass exposed to the impact of vehicular traffic have increased levels of Pd, from 10.9 to 129 µg/kg, at the distance of 5 and 0 m from the road, respectively. However, there was not observed any relationship with its concentration in soils (Hooda et al., 2007). Ryegrass sampled along highways in France contain Pd within the range of 1.5–6.8 µg/kg (Dan-Badjo et al., 2007).

Fuchs and Rose²⁴⁸ suggested a significant Pd mobility in the organic cycle, and thus its phytoavailability. These authors gave the range of Pd in limber pine to range from 2 to 285 µg/kg (AW). Kothny⁴¹⁶ found Pd in leaves and twigs of various trees to range from 30 to 400 µg/kg (AW) and reported a great seasonal variation of its concretions in leaves under different climatic conditions and stages of plant growth.

Farago and Parsons⁹⁹¹ reported that Pd is relatively toxic to water hyacinth which has a strong ability for its accumulation. Uptake of Pd by barley from nutrient solution depends on Pd particle diameter. Stress effects of Pd in plants was observed at a lower concentration compared with Pt and Rh (Battke et al., 2008). Pd is likely to be bound to high molecular-weight proteins and is able to replace Mn in some metalloenzymes due to similar ionic radii.⁴¹⁶ Phytotoxic effects in terrestrial plants at Pd concentrations from about 2 to 60 mg/L of the nutrient solution were reported (UNEP/WHO, 2002). However, Smith et al.⁷⁴³ gave a lower phytotoxic Pd concentration, within the range 1–3 mg/L, that affected in a damage to the structural units of cells. The inhibition of some metabolic processes has also been observed under increased Pd content in plant tissues. Kovalevskiy et al. (2006) studied a formation of Pt-microbioliths in plants grown in Pd-enrichment soil.

TABLE 15.7
Mean Pd Contents of Food Plants^a (µg/kg FW)

Plants	Pd
Cereals, miscellaneous	0.9
Potatoes	0.5
Various vegetables	0.5–0.6
Fresh fruits	0.4
Nuts	3

^a Data from UNEP/WHO (2002).

III PLATINUM

A INTRODUCTION

The average crustal abundance of Pt is given as 4 $\mu\text{g/kg}$ (Table 3.2). Pt abundance in rocks, vary from 0.05 in limestones to 3 $\mu\text{g/kg}$ in ultramafic rocks. As a very nonreactive metal with other elements, Pt occurs mainly in alloys with other PGEs. Its more common minerals are: sperryllite, PtAs_2 ; cooperite, $(\text{Pt},\text{Pd})\text{S}$; braggite, $(\text{Pt},\text{Pd},\text{Ni})\text{S}$; and niggelite, PtSn . Several sulfide minerals, and ilmenite, zircon, gadolinite, are possible hosts for Pt which has an approximate range of concentrations from 0.2 to 2 mg/kg . According to Finkelman (1999), the arithmetic mean of Pt in the United States coal is $<1 \mu\text{g/kg}$, whereas Li (2000) reported 230 $\mu\text{g/kg}$ in the reference coal sample (SRM1632).

The annual global production of Pt in 2008 was 200 t (USDI, 2009). The highest proportion of Pt is presently used in VECs and for jewelry. Recently designed TWCs systems for vehicles contain 0.08% Pt (Hoffman *vide* Ravindra et al., 2004). Pt is also broadly used in various industries, mainly as catalyst in chemical processes. In various alloys, Pt is used in dentistry and in medicine for neurological prostheses and some long-term electrode implantations. There is a growing application of Pt complexes (e.g., cisplatin) as effective drugs for treating various tumors and carcinomas. Effluents of some hospitals are considered now as a main Pt source in sewage.

B SOILS

The range of Pt mean contents in soils is from 2 to $<40 \mu\text{g/kg}$ and world-soil average is 20 $\mu\text{g/kg}$ (Table 3.2). Swedish arable soils contain Pt at the mean value of 40 $\mu\text{g/kg}$ (Eriksson, 2001). Laterite soils of Australia contain Pt in the range from <5 to 70 $\mu\text{g/kg}$ and its contents of soils from the Napoli metropolitan area vary from 1.6 to 52 $\mu\text{g/kg}$, with the mean value 4.2 $\mu\text{g/kg}$ (Reimann and de Caritat, 1998; Cicchella et al., 2003). The average content of Pt in soils near Sudbury, an industrial region of Canada, is $<0.8 \mu\text{g/kg}$ (WHO/IPCS, 1991). Farago et al. (1998) presented mean concentrations of Pt in soils and road dust in the United Kingdom from 2.29 to 20.8 $\mu\text{g/kg}$, and in soils of botanic garden, from 0.8 to 1.6 $\mu\text{g/kg}$. Fuchs and Rose²⁴⁸ reported the Pt content of surface silty soils to range from <20 to 75 $\mu\text{g/kg}$, being the highest in the soil over weathered norite. The magnetic fraction of these soils seemed to contain most of Pt, from <860 to $<3000 \mu\text{g/kg}$.

The Pt distribution in surface soils shows positive correlation with traffic flow. Its highest concentrations in soils occur directly at the edge of the motorway and decrease with increasing distance from the highway. Maximum levels of Pt was reported for roadside soils of various countries, as follows (in $\mu\text{g/kg}$): (1) Western Australia, 440 (Whiteley, 2005); (2) Germany, 330 (Ravindra et al., 2004), and 50.4 (Wichmann et al., 2007); (3) Athens, 141 (Riga-Karandinos et al., 2006); (4) Mexico City, 300 (Morton et al., 2001); (5) Paolo, Hawaii, 506 (Sutherland et al., 2007); and (6) Campania region, Italy, 278 (Cicchella et al., 2008). Roadside soil samples from Austria contained Pt within the range of 0.16–134 $\mu\text{g/kg}$, while the background content was estimated at 0.4 $\mu\text{g/kg}$ (Fritsche and Meisel, 2004).

Low levels of Pt, 0.3–17 $\mu\text{g/kg}$ in roadside soils from Sao Paulo (Brazil) resulted from the different Pt/Pd ratio in automobile catalytic converters (Morcelli et al., 2005). Roadside dust sampled from freeways with heavy traffic in San Diego contain higher amounts of Pt, up to 680 $\mu\text{g/kg}$ (Hodge and Stallard *vide* Ravindra et al., 2004).

The estimation of Pt emission from traffic varies and recent calculations showed that it might be between 0.5 and 0.8 $\mu\text{g/km}$ (Pyrzyńska, 2000). Based on Pt concentrations found in soils near roadsides and on volumes of traffic, Zereini et al. (2001) calculated this value at an average of 0.27 $\mu\text{g/km}$ in the vicinity of Frankfurt, Germany. Although Pt emitted from VECs is mainly in the form of nanocrystals of metallic Pt, some oxidized species were identified (Nachtigall et al. *vide* Pyrzyńska, 2000). Such Pt species could be easily mobilized by complexation, particularly when complexed with chlorides and OM (HA, FA) and undergo biotransformation (e.g., biomethylation). According to Colombo et al. (2008), Pt is likely to form complexes with some inorganic ions (Cl, N, S) that

contribute to its mobility in environmental and biological systems. Increased Cl levels, especially in soil solution, promote the Pt mobility (WHO/IPCS, 1991). According to Ljubomirova et al. (2008) only up to 5% of Pt in street dust is mobile fraction.

Sewage sludge from municipal purification plants might be a serious source of Pt, mainly due to its great discharge from some hospitals. Its concentrations in hospital effluents range widely from <10 ng/L for the Belgian and Italian hospitals to ca. 3.5 µg/L for the Austrian and German hospitals (Ravindra et al., 2004). In the communal sewage might be diluted up to <10 ng/L. It was concluded that the main Pt input into sewage originates rather from urban and road-off dust than from hospital sewage.

The Ni industry (e.g., on the Kola Peninsula) may also be a significant Pt source in soils (Niskavaara et al., 2004).

C PLANTS

Although Pt is strongly held in soils, apparently plants easily take up mobile complexes of Pt, associated mainly with SOM. Pyrzyńska (2000) cited, after Helmers, that values of the TF for Pt, from soil to plants, are relatively high and similar to those for Cu. Pt²⁺ complexes are easily taken up by plants and are accumulated mainly in the roots. Several Pt-binding proteins were isolated from plants (Hoppstock and Sures, 2004). Farago and Parsons⁹⁹¹ described the high phytotoxicity of this metal, with Pt⁴⁺ species being less toxic than those of Pt²⁺.

Grasses from remote locations contain Pt in the range of 0.2–0.5 µg/kg (Hoppstock and Sures, 2004), whereas from road perimeter have much higher Pt levels. Grass samples collected from rural areas contained Pt within the range 0.1–0.3 µg/kg, and from areas exposed to traffic, 0.8–3.0 µg/kg (Ravindra et al., 2004).

According to Leiterer et al. (2004), a main part of Pt emitted from VECs is deposited as suspended particles on the plant surface. Some plants collected from the roadside in France are reported to contain 100–830 µg Pt/kg (Cabrera et al., 1996). According to these authors, mean Pt concentration of wine from different regions of France averages around 10 µg/L and does not represent any imminent toxicological risk. The lowest Pt contents is reported in cereal grains of Sweden, whereas its quite elevated levels are in corn grains from Austria (Table 15.8).

TABLE 15.8
Platinum in Plants from Various Countries^a (µg/kg)

Sample	Country	Pt
Corn, grains	Austria	642
	Germany	80
Wheat/barley, grains ^b	Sweden	0.2; 0.9
Radish, roots	Germany	530
Bean, leaves	Belgium	3.76
	Germany	1.5–550 ^c
Tobacco, leaves	Germany	23,300
Roadside grass	Belgium	1.4–1.7
	Germany	17–96 ^d

^a From various sources, as compiled by Ravindra et al. (2004), unless otherwise stated.

^b After Eriksson (2001).

^c Treated with car exhaust.

^d Hees et al. *vide* Pyrzyńska (2000).

Tree bark contain variable amounts of Pt, from 0.07 to 38 µg/kg, sampled from remote sites and urban areas, respectively, whereas pine needles from urban areas have Pt up to 102 µg/kg (Ravindra et al., 2004). Moss (*Pleurozium schreberi*) sampled from high-traffic region in Finland contain Pt up to 12.2 µg/kg (Niemela et al., 2007). Increased content of Pt (and Pd) in moss samples from the vicinity of the Ni industry on the Kola Peninsula provides evidence that PGEs are emitted to the environment (Niskavaara et al., 2004). Shacklette et al.⁷¹⁰ gave the range in Pt concentrations in herbage growing on metamorphic and Pt-bearing ultramafic rocks to be from 3500 to 6600 µg/kg (AW).

16 Elements of Group 11 (Previously Group Ib)

The Group 11 is composed of copper (Cu), silver (Ag), and gold (Au). Ag and Au belong to the so-called noble metals. All these metals occur in variable oxidation stages, mainly +1 and +2 (Table 16.1). Cu and Ag reveal chalcophilic tendencies whereas Au is siderophilic. The terrestrial abundance of Cu is very well documented, whereas data for Ag and Au occurrence are rather scarce (Table 16.1).

For nearly nine millennia, Cu and Au were the only metals known to man, and Cu has been mined for more than 6000 years. Thus, these metals are very closely associated with the progress of human civilization. Cu was known already at the end of Stone Age and has been used by human beings since 4000 BC. Romans exploited Cu from the island Cyprus, and the metal was named after the island as *cuprum*.

I COPPER

A INTRODUCTION

Copper occurs in the Earth's crust at concentrations between 25 and 75 mg/kg, average 55 mg/kg (Table 3.2). Its abundance pattern in rocks shows the tendency for the concentration in mafic igneous rocks and in argillaceous sediments (Table 16.2).

Copper reveals a strong affinity for sulfur, hence its principal minerals are chalcopyrite, CuFeS_2 ; bornite, Cu_5FeS_4 ; chalcocite, Cu_2S ; and covellite, CuS . During the weathering of copper sulfides, Cu is incorporated in oxide and carbonate minerals of which cuprite, Cu_2O ; tenarite, CuO ; malachite, $\text{Cu}_2\text{CO}_3(\text{OH})_2$; and azurite, $\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$ are the most common. Cu is often associated with sphalerite, ZnS ; pyrite, FeS ; and galena, PbS . Its ores are commonly found in acid igneous rocks and various sedimentary deposits.

World Cu production has increased steadily (in Mt): 9.9 in 1995, 13.7 in 2003 (USGS, 2004), and 15.7 in 2008 (USDI, 2009). Due to versatile properties, Cu has a wide range of applications. It is used for the production of various conductor materials (e.g., fertilizers, pesticides). Due to its bacteriostatic properties, it is added to animal fodder.

B SOILS

The general values for the average total Cu contents in soils of different groups all over the world range between 14 and 109 mg/kg (Table 3.2). Contents of Cu are closely associated with soil texture and usually are the lowest in light sandy soils and the highest in loamy soils (Figure 16.1, Table 16.2). The regularity in large-scale Cu occurrence in soils indicates that two main factors, parent material and soil formation processes, govern the initial Cu status of soils. Also, the clay fraction contributes significantly to the Cu content of soils. As the RDI value indicates, this is a main soil parameter influencing Cu soil status (Figure 16.2). Other soil properties, such as Fe and Mn oxides, and base saturation, explain about 15–25% of all impact factors.

The Cu geometric mean of more than 32,000 agricultural soil samples of Poland is only 6.5 mg/kg, which is due to the predomination of light sandy acid soils.¹⁵¹⁴ The baseline levels for Cu in soils of Brazil is given (in mg/kg) as 1.0 and 8.7 for sandstone and limestone soils, respectively (Melo et al.,

TABLE 16.1
Selected Properties of Trace Metals of Group 11

Element	Atomic Number	Atomic Weight	Ionic Radii ^a (pm)	Oxidation State ^b	Density (g/cm ³)
Cu, copper	29	63.54	60–91	+1, +2	8.92
Ag, silver	47	107.87	81–142	+1 , +2, +3	10.5
Au, gold	79	196.97	71–151	0, +1, +3 ^c	19.3

^a Approximate average values for the main oxidation states.

^b Valence values in bold are for main oxidation states.

^c Oxidation states +2 and +5 are also reported.

2006). The concentration of Cu in 3045 samples of surface soil from major agricultural production areas of the United States varies from <0.6 to 495 mg/kg (geometric mean, 18 mg/kg).¹³²⁹ Range for Cu in soils of South Africa is given as 3–117 mg/kg, at established MTL value as 100 mg/kg (Herselman et al., 2005). Relatively high Cu contents, up to 22,360 mg/kg (at average 17 mg/kg), are reported for some top soils of the Slovak Republic (Čurlik and Šefčík, 1999).

Generally, Cu is accumulated in the upper few centimeters of soils, however, due to its tendency to be adsorbed by SOM, carbonates, clay minerals, and oxyhydroxides of Mn and Fe, it may be also accumulated in deeper soil layers. Especially HA are reported to reveal a large binding capacity for this metal (Logan et al., 1997). Cu is a rather immobile element in soils and shows relatively little variation in total contents of soil profiles (Figure 16.1). The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons. This phenomenon is an effect of various factors, but above all, Cu concentration in surface soils reflects its bioaccumulation as well as its anthropogenic sources.

TABLE 16.2
Abundance of Trace Elements of Group 11 in Rocks and Soils

Rock/Soil	Cu (mg/kg)	Ag (mg/kg)	Au (μg/kg)
Earth's crust	25–27	0.07–0.08	3–4
Igneous rocks	—	—	—
Ultramafic	10–40	0.05–0.06	5
Mafic	10–120	0.07–0.1	0.5–5
Acid	5–30	0.05–0.07	1.2–1.8
Sedimentary rocks	—	—	—
Argillaceous	40–60	0.07–0.1	2.5–4
Sandstones	5–30	0.05–0.25	3–7
Calcareous	5–10	0.1–0.15	2–6
Soils ^a	38.9 ^b	0.13 ^b	3 ^b
Arenosols (sandy)	3–30	—	1–5
Podzols (medium loamy)	7–70	0.06–0.4	—
Cambisols (heavy loamy)	7–140	—	—
Calcisols (calcareous)	10–70	—	—
Histosols (organic)	10–100	2–5	1–8

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil average (Table 3.2).

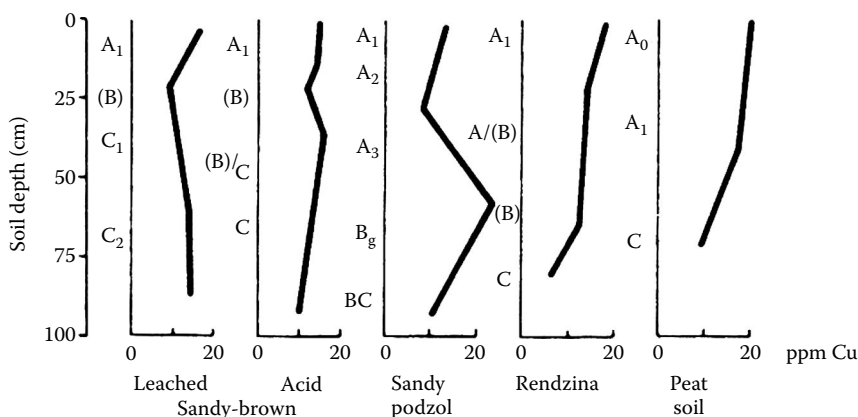


FIGURE 16.1 Distribution of Cu in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

Copper occurs in most soils as the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion adsorbed on clay minerals or coprecipitated on other mineral and organic soil components. Depending upon soil pH, Cu may occur in various forms: Cu^{2+} , Cu^+ , $\text{Cu}(\text{Cl}_2)^-$, CuSO_4^0 , $\text{Cu}(\text{OH})_2^0$, CuCO_3^0 , CuCl^0 , and (McBride, 1994; Alloway, 1995). However, in most soils, Cu hydroxides and carbonates are likely to predominate (Figure 16.3).

Influence of pH on the Cu mobility in soils depends highly on its compounds and species (Figure 16.4). Concentrations of Cu in soil solution range from 0.5 to 135 $\mu\text{g/L}$, depending on techniques used and on soil types. In soil solution it may occur as cations: Cu^{2+} , CuOH^+ , $\text{Cu}_2(\text{OH})_2^{2+}$, and as anions: $\text{Cu}(\text{OH})_3^-$, $\text{Cu}(\text{OH})_4^{2-}$, and $\text{Cu}(\text{CO}_3)_2^{2-}$ (Kabata-Pendias and Sadurski, 2004). Ponizovsky et al. (2006) calculated that most of the added Cu is sorbed in soil, and only about 1% of the total amount remained in soil solution. These authors adapted a model for a prediction of dissolved Cu concentration in soils at low moisture content.

According to Ponizovsky et al. (2006), main variables affecting the Cu mobility are: SOM, DOM, pH, and Cu soil content. Overall solubility of both cationic and anionic forms of Cu decreases at about pH 7–8. It was estimated that hydrolysis products of $\text{Cu}(\text{CuOH})^+$ and $\text{Cu}_{2(\text{OH})_2}^{2+}$ are the most significant species below pH 7, while above pH 8, anionic hydroxy complexes of Cu become important (Figure 16.4). The precipitation of CuCO_3 in calcareous soils is a main process affecting the Cu activity in soil solution (Ponizovsky et al., 2007). As Sanders and Bloomfield⁶⁷⁷ stated, the solubility

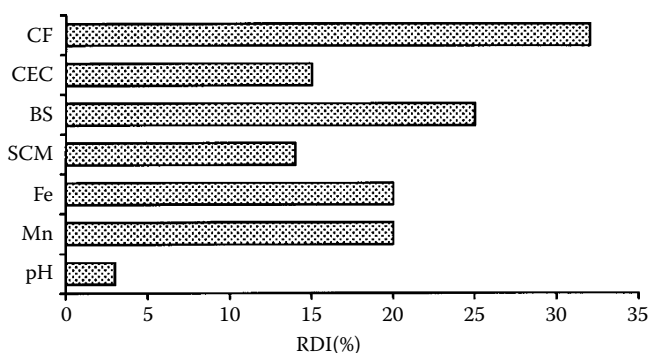


FIGURE 16.2 Relative explanation index (RDI) of statistically significant relationship between Cu and soil parameters in mineral soils at the 99% confidence level (N 5780). Soil parameters: CF—clay fraction <0.02 mm; CEC—cation exchange capacity; BS—base saturation; SOM—soil organic matter; Fe—total content; Mn—total content; pH—in water (soil:water ratio 1:2.5).

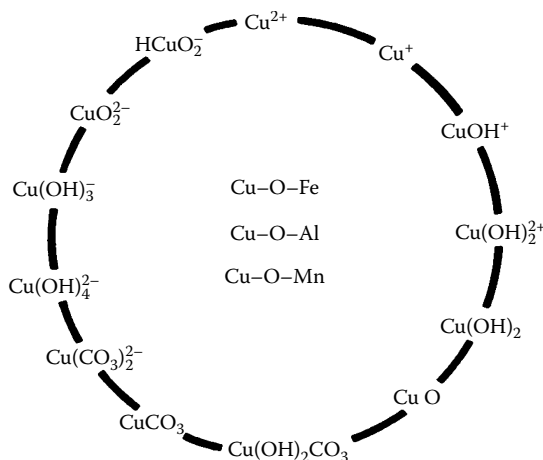


FIGURE 16.3 Ionic species, compounds, and bonds of Cu occurring in soils.

of CuCO_3 is not pH dependent and this compound seems to be a major inorganic soluble form of Cu in neutral and alkaline soil solutions, while nitrate, chloride, and sulfate do not complex a significant portion of Cu in the soil solution. However, the most common forms of Cu in soil solutions are soluble organic chelates of this metal. Although very little is known about kinds of soluble organic Cu species, about 80% of these forms were estimated to be organic chelates.³²⁰ McBride and Blasiak⁵¹⁹ reported that due to a great affinity of Cu for organic complexing, soluble Cu-organic forms appear to comprise most of the Cu solution over a wide range of pH. Organic complexing of Cu has a prominent practical implication in governing the bioavailability and the migration of Cu in soils.

The bioavailability of soluble forms of Cu depends most probably on both the molecular weight of Cu complexes and on the amounts present. Compounds of a low molecular weight liberated during decay of plant and animal residues as well as those applied with sewage sludge may greatly increase the availability of Cu to plants. It should be emphasized, however, that concentrations of Cu in soil solutions are principally controlled by both the reactions of Cu with active groups at the

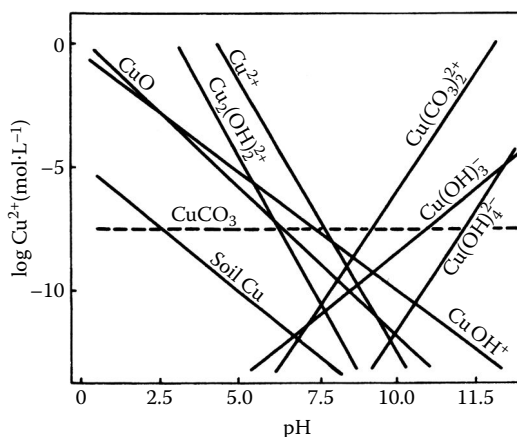


FIGURE 16.4 Schematic diagram of solubility of Cu ionic species and Cu compounds in soil. (Data compiled from Lindsay, W. L., *Micronutrients in Agriculture*, Mortvedt, J. J., Giordano, P. M., and Lindsay, W. L., eds., Soil Science Society of America, Madison, WI, 41, 1972a; McBride, M. B., *Copper in Soils and Plants*, Loeragan, J. F., Robson, A. D., and Graham, R. D., eds., Academic Press, New York, 25, 1981.)

surface of the solid phase and by reactions of Cu with specific substances. Shi et al. (2005) studied kinetics of Cu release from soils and concluded that desorption is the main process contributing metal to the solution.

The behavior, phytoavailability and toxicity of Cu are influenced by its species, and are not a function of its total concentration (Allen, 1993). Several soil variables control the Cu solubility and thus bioavailability; these include: pH, oxidation and reduction potential, SOM, soil texture, mineral composition, temperature, and water regime. The mobility of Cu is especially reduced at the presence of large mineral colloids with Fe–Al-oxyhydroxide coatings, by oxyhydroxide particles of Al, Mn, Fe, and by OM (Kabata-Pendias and Sadurski, 2004). DOM has a great affinity to fix Cu and thus to inhibit its sorption in soils. These phenomena are attributed to the formation of soluble Cu-organic complexes (Zhou and Wong, 2003). In mineral soils, natural attenuation of Cu occurs as an effect of Cu substituting for Ca in calcites present in calcareous soils and as precipitation of $\text{Cu}(\text{OH})_2$ and/or $\text{Cu}_2(\text{OH})_2\text{CO}_3$ in other soils (Ma et al., 2006). Wei et al. (2007) observed that the long-term application of Cu fertilizers resulted in a great Cu accumulation in surface soil (0–15 cm) due to its low mobility, since a great proportion of added Cu was bound to mineral soil fractions. The Cu balance in surface soils of different ecosystems presented in Table 3.13 shows clearly that the atmospheric input of this metal may partly replace the removal of Cu by biomass production and in some cases may even exceed its total output from soils.

The Cu deficiency in crop plants due to low contents of Cu in soils has been reported for many countries since the nineteenth century (Alloway, 1995). However, Cu deficiency in world agriculture is also closely associated with soil conditions and management practices. Copper deficiency most commonly occurs in soils which are: (1) coarse structured and high pH, (2) formed from calcareous parent material, and (3) rich in organic matter. Thus, the deficiency can be a consequence of the low content of total soil Cu, or the condition of the soil reducing the mobility and thus availability of Cu. Among different extractants used for the diagnosis of Cu deficiency, the solution of AAACEDTA has been recently used most commonly, however EDTA and DTPA also have been used for long time. The interpretation of these values has been broadly discussed by Alloway (2005). Very high correlation was found between aqua regia (pseudo total) Cu and DTPA-soluble Cu, while very low correlation was found between CaCl_2 and aqua regia or DTPA-soluble Cu.¹²⁷⁶ However, it may be generally stated that total Cu contents below 10 mg/kg in different soils may indicate deficiency.

Many authors have reported that Cu can be adsorbed by minerals within the range from 0.001 to 1 mM/L or from 30 to 1000 mM/g. The greatest amounts of adsorbed Cu have always been found for Fe and Mn oxides (hematite, goethite, birnessite), amorphous Fe and Al hydroxides, and clays (montmorillonite, vermiculite, imogolite). Harter³⁰⁷ reported that the most significant correlation was obtained between Cu adsorption and the sum of bases for the surface soils, while in the subsurface horizons the adsorption of Cu was highly related to vermiculite content.

The ability of the organic soil constituents to bind Cu is well-recognized, and there are a tremendous number of comprehensive publications on this subject. Stevenson and Fitch⁷⁵⁸ stated that the maximum amount of Cu^{2+} that can be bound to HA and FA acids is approximately equal to the content of acidic functional groups. In general, this corresponds to the sorption of from 48 to 160 mg of Cu per gram of HA. Organic binding of Cu in soils differs to some extent from that described for other divalent ions. According to Bloom and McBride⁸⁰ and Bloomfield,⁸¹ peat and HA strongly immobilize the Cu^{2+} ion in direct coordination with functional oxygens of the organic substances. Ponizovsky et al.¹⁴⁵⁸ found that the retention of Cu^{2+} by organic-rich soils differs from mechanisms of exchange of alkali and alkali earth metal cations and should be regarded as triple Cu^{2+} , Ca^{2+} , and H^+ cation exchange. Binding of Cu by soils is related to the formation of organic complexes and is highly dependent on soil pH.¹⁵¹¹

To sum up the key role played by OM in the behavior of soil Cu, it can be emphasized that HA and FA are likely to form stable complexes when Cu is present in small amounts and that OM can modify several Cu reactions with inorganic soil components. Microbial fixation plays a prominent role in the binding of Cu in certain surface soils. The amount of Cu fixed by the microbiomass is

widely variable and is affected by various factors, such as metal concentration, soil properties, and growing season (Table 4.10). Microbial fixation of Cu is an important step in the ecological cycling of this metal.

1 Soil Contamination

Soil contamination by Cu compounds has been the subject of detailed studies for several decades and a large database has been already collected and presented in a number of monographs and papers. Several significant sources such as fertilizers, sewage sludge, manures, agrochemicals, industrial by-product wastes, and the quality of irrigation waters have contributed to increased Cu levels to agricultural soils. Highly increased levels of Cu are observed in soils surrounding Cu mines and smelters (Table 16.3). As Cu is only slightly mobile under most soil conditions elevated contents may persist for a long time (Hutchinson, 1979).

Some local or incidental Cu input to soils may arise from corrosion of Cu alloy construction materials (e.g., electric wires, pipes). Major sources of pollution (mainly nonferrous metal smelters) present halos in which Cu concentrations in surface soils decrease with distance, which is especially pronounced in a downwind direction (Figure 16.5). While main point sources of industrial pollution have a local environmental impact, they also contribute to the global long-distance pollution of the atmosphere. Airborne fallout of Cu pollutants differs greatly in a specific area and for parts of the continents, being the greatest in central Europe. Heindrichs and Mayer³¹⁰ reported the atmospheric input of Cu to be 224 g/ha/year for Germany, which is, comparatively, the highest value (Table 3.13).

Contamination of soil by Cu compounds results also from utilization of Cu-containing material such as fertilizers, sprays, and agricultural or municipal wastes. Input of Cu to soils of livestock farms in the EU member countries vary greatly (in g/ha/year): from 29 in Czech Republic to 2771 in Italy. Minus load charges were calculated only for Switzerland (−17) and for Norway (−138). Cu balance in crop farms is much lower and in several countries show some loss of Cu from top soils, up to 54 g/ha/year in Norway. However, the balance of Cu for vineyard soils and sludged soils of Italy have been estimated at 13,923 and 3905 (g/ha/year) respectively (Eckel et al., 2005). Fernandez-Calvino et al. (2008) reported that increased Cu levels in vineyard soils up to 246 mg/kg affected the Cu accumulation up to 209 mg/kg in river sediments. In the surface soil layer of vineyards, after 50–100 years of applied fungicides, the content of Cu forms dissolved by various extractants were as follows (in mg/kg): aqua regia 220, DTPA 82.5, and CaCl₂ 0.23.¹²⁷⁶ As a result of using a Cu-sulfate fungicide (Bordeaux mixture) for more than 100 years, Cu concentrations in top vineyard soils in France vary from 100 to 1500 mg/kg.¹²²⁵ Also a high Cu content, up to 1400 mg/kg was in vineyard soils amended with poultry litter (Nachtigall et al., 2007).

The maximum allowable loading of Cu with wastes to arable soils of the EU countries is estimated at 12 kg/ha/year. Ranges of MAC values commonly cited in literature range from 20 to 100 mg/kg (Kabata-Pendias and Sadurski, 2004). Precautionary values for Cu in Germany are established for soils of various texture as follow (in mg Cu/kg): clay, 100; loam, 60; and sand, 30 (Eckel et al., 2005).

Tiller and Merry⁷⁹⁵ reviewed all basic problems of Cu behavior in contaminated soils and the assessment of the environmental impacts. Mingelgrin and Biggar¹⁰⁹³ studied the behavior of Cu species in sewage sludge under various conditions and observed that the increase of easily soluble Cu in sludge applied to soils can be a source of Cu contaminations of plants, and in some cases also of groundwater (Table 16.3). In sewage sludge-treated soil, Cu accumulations up to 1170 mg/kg was reported.¹²⁶⁴

The most important statement on Cu contamination of soils is the great affinity of surface soils to accumulate this metal. As a consequence, Cu content of soils has already been built up to the extremely high concentrations up to above 4000 mg/kg Cu from industrial sources of pollution and of about 1500 mg/kg Cu from agricultural origins of the metal (Table 16.3).

Among various methods used to remediate Cu-contaminated soils, a relatively common technique is immobilization by OM. For example, Kikkilä (2002) studied the remediation techniques for

TABLE 16.3
Copper Contamination in Surface Soils (mg/kg)

Site and Pollution Source	Country	Mean or Range of Content	Reference
Old mining area	UK	13–2000	166, 915, 959
Deactivated Cu ore plant	Brazil	2140	Cassella et al. (2007)
Nonferrous metal mining	UK	415–733	166
	Japan	456–2020	395
Metal-processing industry	Australia	847	57
	Belgium	16–1089	1142
	Bulgaria	24–2015	774
	Canada	1400–3700 ^a	245
	Japan	26–206 ^b	926
	Poland	72–620	380, 1014
	Romania	1387	1126
	Russia ^f	121–4622	1217
Urban gardens, orchards, and parks	Australia	210	795
	Canada	11–130	332
	Japan	31–300	395
	Philippines	352	1178
	Poland	12–240	159
	U.S.	3–140	628
	Russia	50–83 ^c	394
Sludged, irrigated, or fertilized farmland	Holland	265	314
	UK	40–800	959, 1134
	Poland	80–1600	682
	U.S.	58–130 ^d	1186
	Germany	187–280	176
	Galicja, Spain	273–5241	Álvarez et al. (2003)
Application of fungicides	Germany	273–522	652
	UK	60–380	959
	Kenya	883 ^e	1059
Vineyard soils	France	100–1500	Besnard et al. (1999)
Military shooting range	Swiss	996–6200 ^g	Robinson et al. (2008)

^a For 3–6.3 km distance from a smelter.

^b Paddy soils.

^c Vineyard.

^d Plot experiment, 9 years after sludge addition 33–180 t/ha, respectively.

^e Coffee plantation.

^f Up to 10 km distance from the smelter on Kola Peninsula.

^g Geometric mean for rhizospheric soil.

polluted soils, 0.5 km away from a Cu–Ni smelter in Finland, by mulching with OM (mixture of compost and woodchips). The organic mixture converted the Cu into less exchangeable and thus less bioavailable forms. This technique has resulted in a low Cu in soil solution and in the subsequent reduction of toxic effects on microbiota. According to Kumpiene et al. (2008), amendments effective in the Cu immobilization are clays, carbonates, and Fe oxides. Ling et al. (2007) emphasized effective Cu-sorption of bentonite within a wide pH range of 2.5–7.0. Vega et al. (2007) described that clay soil fraction contributes significantly to the Cu sorption due to its vermiculite content.

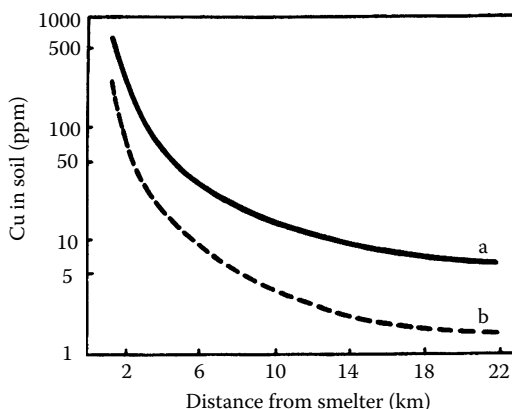


FIGURE 16.5 Smoothed patterns for Cu concentrations in soils as a function of downwind distance from a Cu smelter (mean values of 3 years); (a), total content; (b), soluble content. (Based on Kabata-Pendias, A., Bolibrzuch, E., and Tarlowski, P., *Rocz. Glebozn.*, 32, 207, 1981.)

The amelioration techniques based mainly on the addition of lime, peat (OM), and phosphate to soils bring variable effects related to soil and plant factors. It should, however, be kept in mind that Cu stored in surface soils influences their biological activity and may become available to plants under various conditions. According to results of the experiment carried out by Boon et al.¹²³⁶ planting a Cu-tolerant grass (*Agrostis capillaris* L.) on Cu-contaminated acid soil (750 kg Cu/ha) can significantly increase the biological activity of a soil.

Various microorganisms are known for their resistance to high Cu concentrations. Zabawski and Boratyński¹¹⁹⁵ reported that *Penicillium* species may accumulate Cu up to about 20,000 mg/kg, from the solution containing Cu at 100 mg/kg. Micromycetes seem to develop resistance to Cu in soils contaminated with this metal. *Penicillium* species isolated from the Cu-polluted soil absorbed less Cu and grew better under increased doses of the metal than *Penicillium chrysogenum* isolated from the unpolluted soil (Figure 16.6). Wang et al. (2008a) reported that specific clone of bacteria in the rhizosphere of a Cu-accumulator plant control the availability of this metal. Nanoparticles of Cu at the soil–root interface are formed under impact of endomycorrhizal fungi in oxygenated environments (Manceau et al., 2008).

C PLANTS

1 Absorption and Biochemical Functions

Numerous studies have greatly increased the present knowledge of Cu absorption mechanisms, but they are still far from clear. It may be stated that, however, there is increasing evidence of the active absorption of Cu, passive absorption is likely to occur, especially in the toxic range of this metal in solutions. CF values calculated for oleander and lantana leaves from various sites in Spain vary within the range of 0.08–0.3 and are higher than for other trace metals (Rossini Oliva and Fernandez Espinosa, 2007).

In root tissue, Cu is almost entirely in complexed forms, however, it is most likely that the metal enters root cells in dissociated forms. Graham²⁸⁰ compared the results of different studies carried out on rates of the Cu absorption by higher plant roots and stated that these rates are among the lowest of the essential elements, varying from pico- to $\mu\text{M}/\text{h/g}$ of roots in the physiological concentration range. The rate of Cu uptake by plants, however, widely differs with species of the metal. Grupe and Kuntze¹⁰¹⁹ found that anthropogenic metal (added in the form of Cu oxide) is more available to barley than that of pedogenic origin (Figure 2.2). Bunzl et al. (2001) reported, however, that Cu from slag-contaminated soils was relatively slightly available to vegetables. Despite the great

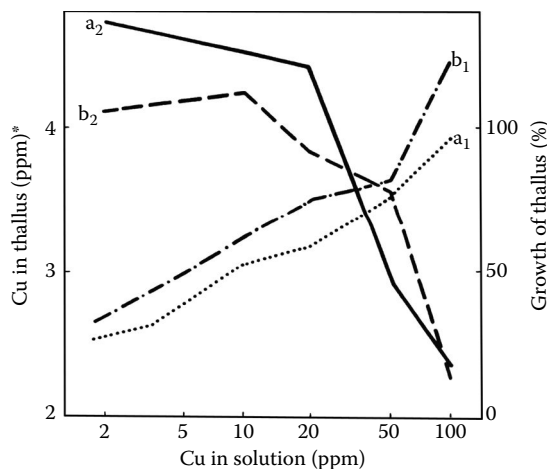


FIGURE 16.6 Copper accumulation and relative growth of thallus of soil micromycetes as a function of the metal concentration in nutrient solution. (a₁) *Penicillium* sp. from soil polluted with Cu—accumulation of metal, (a₂) growth of *Penicillium* sp., relative to control, (b₁) *Penicillium chrysogenum* from unpolluted mineral soil—accumulation of metal, (b₂) growth of *Penicillium chrysogenum*, relative to control. (Modified from Zabawski, J., Boratynski, J., and Płaskowska, E., *Arch. Ochr. Srodowiska*, 1/2, 123, 1987 (Po).) Note: *Values given in powers of ten.

complexity of the absorption mechanisms, a relationship between the concentration of the metal measured in either a nutrient solution or a soil solution and in the soil that supports plants can be observed, especially in the toxic concentration range (Figures 16.7 and 16.8).

The movement of Cu among various parts of plants plays a predominant role in the plant's utilization of Cu. The strong capability of root tissues to hold Cu against the transport to shoots under conditions of both Cu deficiency and Cu excess was observed. Loneragan⁴⁹⁰ and Tiffin⁷⁸⁸ concluded that the excretion of Cu from root cells into xylem and phloem saps where Cu occurs in

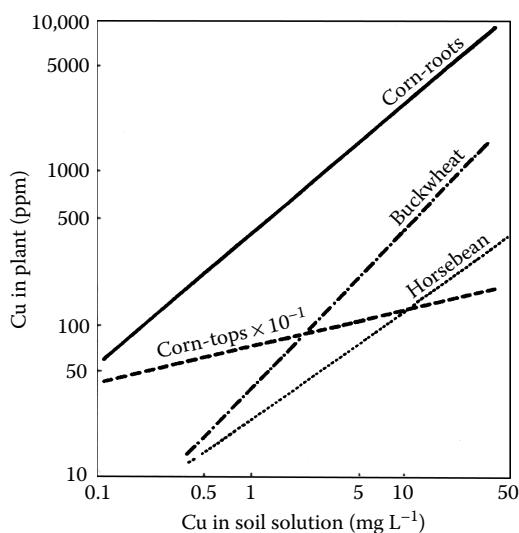


FIGURE 16.7 Relationship between Cu content of plants and its concentration in soil solution obtained from Cu-contaminated soils. (From Kabata-Pendias, A. and Gondek, B., *Trace Subst. Environ. Health*, Vol. 12, Hemphill, D. D., ed., University of Missouri, Columbia MO, 523, 1978. With permission.)

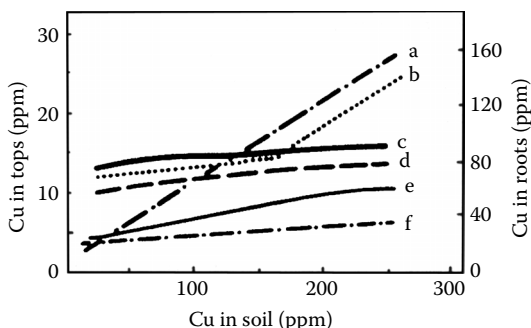


FIGURE 16.8 Cu uptake by plants and organs from Cu-contaminated soils. (a) Valencia orange roots; (b) potato stalks; (c) pasture herbage; (d) lettuce leaves; (e) barley grains; (f) wheat grains. (Data compiled from Diez, Th. and Rosopulo, A., *Sonderdruck Landw. Forsch.*, 33, 236, 1976; Fiskell, J. G. A. and Brams, A., *Soil Crop Sci. Soc. Fla.*, 25, 128, 1965; Thoresby, P. and Thornton, I., *Trace Subst. Environ. Health*, Vol. 13, Hemphill, D. D., ed., University of Missouri, Columbia, MO, 93, 1979.)

mobile forms is a key process in the Cu nutrition of plants. The concentrations of Cu in xylem and phloem saps range from traces to 140 μM and seem to correlate with the concentrations of amino acids. The Cu mobility within plant tissues strongly depends on the level of Cu supply, being the highest with a “luxury” supply.⁴⁹⁰ However, Cu has low mobility relative to other elements in plants and most of this metal appears to remain in root and leaf tissues until they senesce; only small amounts may move to young organs. Therefore, the young organs are usually the first to develop symptoms of Cu deficiency.

A considerable proportion of the Cu present in green tissues appears to be bound in plastocyanin and in some protein fractions. There is also a tendency to accumulate Cu in reproductive organs of plants; this, however, differs widely among plant species. The highest concentrations of Cu have been found in the embryo of cereal grains and in the seed coat. Loneragan⁴⁹⁰ cited Cu concentration to be (in mg/kg) from 2 to 18 in the embryo, and from 8 to 23 in the seed coat, while in whole seeds the highest value was 4. These proportions do not correspond closely to those reported by Liu et al.,⁴⁸⁴ who found a more uniform distribution of Cu throughout the barley grain.

Copper, the essential metal in plants, is a constituent of several “key” enzymes, and also plays important functions in physiological processes, such as:

- Photosynthesis and respiration
- Carbohydrate and nitrate metabolisms
- Water permeability
- Reproduction
- Disease resistance

The deficiency of Cu strongly affects physiological processes and therefore plant production. Cu-deficiency in crops is widespread and often it is in a hidden form. As Alloway (2005) stated this form of Cu-deficiency is the most ubiquitous and economically important, and is a more serious problem in Europe than in many other parts of the world. This is associated mainly with soil kinds (Table 16.4), climatic conditions, and crops grown. Common crop plants that are highly sensitive to Cu deficiency are: wheat, oats, sunflower, alfalfa, carrots, lettuce, spinach, onion, and citrus trees.

Copper is slightly mobile in plants as it is strongly bound by nitrogen and proteins. With Cu-deficiency, a plant may grow normal vegetation for a short time, but there will be a failure in the redistribution of Cu from old leaves and roots causing chlorosis and tip necrosis in new leaves, known as Cu-deficiency symptoms.

TABLE 16.4
Variation in Cu Content of Red Clover (Bud Stage) and Timothy
(Immature Stage) as Influenced by Soil Factors (mg/kg)

Soil Parent Material	Red Clover ³²		Timothy ³⁸⁸
	Meadow	Cultivated Field	
Phyllite	11.1	11.3	—
Porphyry	11.5	10.2	—
Basalt	9.6	10.0	—
Loess or silt	9.7	9.8	4.1
Granite	9.2	9.7	—
Alluvial loamy deposit	9.0	9.8	4.8
Diluvial sand	8.4	8.1	3.9
Glacial till	8.5	7.5	4.0
Moor and peat	6.4	6.3	4.0

Very extensive studies have been made on the forms and behavior of Cu in plants. All findings described in a number of outstanding textbooks can be summarized as follows:

- Cu is mainly complexed with organic compounds of low molecular weight and with proteins.
- Cu occurs in the compounds with no known functions as well as in enzymes having vital functions in plant metabolism.
- Cu plays a significant role in several physiological processes—photosynthesis, respiration, carbohydrate distribution, N reduction and fixation, protein metabolism, and cell wall metabolism.
- Cu influences water permeability of xylem vessels and thus controls water relationships.
- Cu controls the production of DNA and RNA, and its deficiency greatly inhibits the reproduction of plants (reduced seed production, pollen sterility).
- Cu is involved in the mechanisms of disease resistance. This resistance of plants to fungal diseases is likely to be related to an adequate Cu supply. There is also evidence that plants with enriched Cu concentrations are susceptible to some diseases. These phenomena may indicate that the role of Cu in disease resistance is an indirect one.

The most important practical implications are related to deficiency and toxicity of Cu. Deficiency affects physiological processes and therefore plant production. However, as Bussler¹¹⁵ stated, in most of the processes affected by the Cu deficiency the shortage of Cu operates indirectly. This explains the difficulties in the assessment of Cu needs and Cu availability to plants. The Cu-deficient concentration in the nutrient solution for cereal growth is given as 5 mg/L.³¹⁷ Jewell et al.¹⁰³⁹ grew Cu-deficient barley at the level of about 1 mg/L (12.5 ng/cm³). These authors observed a high irregularity in both pollen development and fertility and described some reorganization of nuclear structure.

Although the Cu deficiency is widespread (Table 5.11) and has long been known, diagnosis and correction of the deficiency still need more study. Different methods have been applied to diagnosis using plant symptoms, soil testing, or biochemical assays. However, when these approaches are used individually, results are crop and soil specific that the development of a universal test seems unlikely. Robson and Reuter,⁶⁶⁰ Gartrell et al.,²⁵⁸ and Mengel and Kirkby⁵³¹ suggested that the tissue test should be considered together with other relevant information (field observations, soil analysis, etc.) for the most accurate assessment of the need for Cu applications.

The Cu-deficiency levels in plants show large genetic differences, however, some generalizations as presented in Table 5.8, indicate that Cu levels less than 2 mg/kg are likely to be inadequate for most plants. The threshold contents of Cu in soils that were established using different procedures differ widely and their use is not encouraged for the determination of Cu deficiency for various crops.

Removal of Cu by crops is negligible when compared to its content in soil. An average cereal crop removes Cu in amounts of about 20–30 g/ha, whereas forest biomass removes about 40 g/ha/year. Gartrell²⁵⁷ pointed out that comparing the excesses of Cu applied and the amounts removed in farm produce and leached with percolating waters shows that “depletion of soil reserves” is an unlikely explanation for the appearance of Cu deficiency over a short period. Cu application to soils has a long-term effect, and 10 years after Cu fertilization the contents of Cu were still increased in pasture herbage. Repeated Cu applications to soils can lead to toxic concentrations of this metal for some crops. Minnich et al.¹⁰⁹⁴ observed that the Cu concentration in shoot tissues of snap beans increased linearly with the Cu content of the sludge applied, while the Cu content of roots was dramatically increased with both the Cu content and the proportion of sludge in the growth media.

Despite the general Cu tolerance of plant species and genotypes, this metal is considered to be highly toxic. Some inhibitory action of chemical compounds (e.g., methyl jasmonate) on Cu-toxic effects in roots of some plants, especially of dicotyledons, was observed (Maksymiec and Krupa, 2007). General symptoms of the Cu toxicity listed in Table 5.8 show that Cu-induced chlorosis and root malformation are the most common characteristic symptoms of this toxicity. All recent findings can be summarized to show that the decrease of photosynthetic efficiency resulting from Cu-induced destabilization of the photosystem is connected with an inhibition of its donor side and the primary photochemical processes.¹³⁹⁴ The growth depression of sensitive plants was observed at 15–20 mg/kg Cu in tissues,¹⁰⁵² and 10% yield decrease is most likely at Cu concentration within the range of 10–30 mg/kg.¹⁰⁸¹

On the basis of the statements made by Woolhouse and Walker⁸⁸⁶ and Sandmann and Boger,⁶⁷⁸ the processes induced by an excess of Cu²⁺ and Cu⁺ ions may be summarized as follows:

- Tissue damage and elongation of root cells
- Alteration of membrane permeability, causing root leakage of ions (e.g., K⁺, PO₄³⁻) and solutes
- Peroxidation of chloroplast membrane lipids and inhibition of photosynthetic electron transport
- Immobilization of Cu in cell walls, in cell vacuoles, and in nondiffusible Cu-protein complexes
- Damage to DNA, and in consequence, inhibition of photosynthetic processes

Functions of some enzymes (e.g., superoxidase, peroxidase, catalase) in leaf tissues were increased under elevated Cu contents and resulted in oxidative stress to plants (Yurekli and Porgali, 2006). Cu–chlorophyll complexes formed in chloroplasts may damage photosynthetic functions (Zvezdanovic et al., 2007). Excess of Cu affected a marked decrease in total root phospholipid levels and other associated compounds resulted in an alteration of membrane permeability and fluidity (Chaffai et al., 2007).

Prediction of the Cu content of soil that results in toxic effects on plants is extremely complex. Before toxic symptoms and yield reductions are evident, the nutritive value of the crops having increased Cu levels seems to create the most significant health risk. A number of observations that Tiller and Merry⁷⁹⁵ reported on the depressed plant growth, especially retarded seed germination and seedling and root development, resulted from an excess Cu concentrations in surface soils. Sonmez (2007) observed that Cu added to soil at the concentration up to 2000 mg/kg decreases biomass of tomato plants and leads to the imbalance of mineral nutrition, reducing uptake of K, Ca, Mg, Fe, and Zn.

In roots or rhizosphere, Cu is in complex form, but its uptake and translocation is a function of the activity of Cu^{2+} . When the total soil concentration of Cu is between 25 and 40 mg/kg below 5.5 pH, then a soil solution level of Cu^{2+} can be toxic to many higher plants (Baker et al., 1994). Hence, soil pH plays an important role in the Cu availability and toxicity to terrestrial plants.

2 Interactions with Other Elements

For optimal development, plants must have not only an appropriate amount of active Cu in cells, but also a balance of chemical elements. Due to the significant functions of Cu in enzymes and its variable valence, ions which have similar affinity as Cu to proteins and other compounds may have antagonistic interrelationships. Many complex interactions of Cu with other elements are observed within plant tissues and also in the external root media, particularly in the uptake-transport processes.

- Cu–Zn interactions are commonly observed.^{280,654} These metals apparently are absorbed by the same mechanism and therefore each may competitively inhibit root absorption of the other.
- Cu–Fe antagonism is indicated as Cu-induced chlorosis. High levels of Cu in a plant decrease the Fe content in chloroplasts.⁶⁴⁷ Fe, on the other hand, reduces Cu absorption from soil solutions, especially in peat soils. The optimal Cu:Fe ratio varies for different plant species. The toxic effects of Cu can be decreased by the addition of Fe. However, a synergistic effect of Cu on Fe absorption by rice seedlings was reported by Kitagishi and Yamane.³⁹⁵
- Cu–Mo interactions are closely related to the N metabolism. The mutual antagonism existing between these elements is highly dependent on plant species and kind of N nutrition. Cu aggravates the Mo deficiency in plants, especially those using N from NO_3 , because Cu interferes with the role of Mo in the enzymatic reduction of NO_3 . Some vegetables are quite susceptible to Mo deficiency if growing in soil with a high level of Cu; and in other plants, the deficiency of Cu is increased with the application of Mo to soil.⁵⁸¹
- Cu–Cd interactions are both antagonistic and synergistic in element uptake by roots. Synergism may be a secondary effect of the damage to membranes due to the imbalanced proportions of the metals.
- Cu–Se interactions are observed mainly as inhibited Cu uptake with increased Se level.
- Cu–Mn interactions are reported to be both synergistic and antagonistic in the uptake processes under defined conditions and at high concentrations of both metals.
- Cu–Ni synergism is observed in similar conditions as Cu–Mn relationships.
- Cu–Cr interrelationships may occur within plant tissues, as well as in external root media. Antagonistic reactions apparently are related to the variable valency of Cr.

Interrelationships between Cu and major elements are quite complex.

- Cu–Al antagonism leads to the reduction of Cu uptake by roots under Al toxic levels, especially in acid soils.
- Cu–N interact in the formation of proteins with Cu complexes; plants with high N levels readily show symptoms of Cu deficiency.
- Cu–P: high P levels in soils reduce mycorrhizal absorption of Cu. An excess of Cu, in contrast, inhibits activity and availability of P.
- Cu–Ca interactions are highly complex and apparently are cross-linked with the range of pH in the growth media. The affinity of carbonates to precipitate Cu is the most common reaction leading to Cu deficiency in soils within the alkaline range of pH or having free CaCO_3 . Liming is the most frequent practice in the amelioration of Cu-contaminated soils. The relatively common occurrences of reduced Cu contents in plants that have an increased supply of some nutrients are often related to secondary effects of Cu dilution resulting from enhanced growth rates of the plant.

Significant information on synergistic interconnections between Cu–F and Cu–Ag in microbial metabolisms were reported by Gadd and Griffiths.²⁵¹

3 Concentrations in Plants

The appropriate content of Cu in plants is essential both for health of the plant and for the nutrient supply to man and animals. Some plant species have a great tolerance to increased concentrations of Cu and can accumulate extremely high amounts of this metal in their tissues (Table 5.9). McGrath¹⁴⁰⁷ described that some 24 Cu hyperaccumulating species have been recorded in various families.

The concentration of Cu in plant tissues seems to be a function of its level in the nutrient solution or in soils (Figures 16.6 and 16.7). The pattern of this relationship, however, differs among plant species and plant parts. Opinions appear to vary considerably as to which factor, soil or plant, affects concentrations of Cu in plant tissues to a higher degree. Anke et al.³² reported a significant variation in Cu uptake by red clover from different soils, while Kähäri and Nissinen³⁸⁸ found fairly uniform Cu levels in timothy from different soils. These authors, however, did not support their results with information on the Cu status of soils (Table 16.4).

Copper contents of various plants from unpolluted regions of different countries range from 1 to XO mg/kg (Tables 16.5 and 16.6). Cu in ash of a variety of plant species, growing under widely ranging natural conditions, is reported to range from 5 to 1500 mg/kg.⁷¹⁰ However, Cu contents of whole plant shoots do not often exceed 20 mg/kg, and thus values from 20 to 100 mg/kg are usually considered to indicate the threshold of excessive contents (Table 5.8). Under both natural and man-induced conditions, the majority of plant species can accumulate much more Cu, especially in roots and storage tissues (Table 16.7). Coffee (*Coffea arabica*) shoots and their brown bark are reported to contain extremely high levels of Cu, up to 4186 mg/kg.¹⁰⁵⁸ The significance of elevated contents of Cu in feed and food plants that reflect man-made pollution needs evaluation from the environmental health point of view.

TABLE 16.5
Mean Levels and Ranges of Cu in Grass and Clover at the Immature Growth Stage from Different Countries (mg/kg)

Country	Grasses		Clovers		Reference
	Range	Mean	Range	Mean	
East Germany	7.4–15.0	10.1	7.6–15.0	10.5	31, 32, 65
Finland	3.8–4.8	4.3	—	—	388
Hungary	3.6–8.4	5.0	4.2–16.2	10.5	803
Japan	1.3–33.1	6.9 ^a	2.0–12.5	6.5 ^b	395
New Zealand	7.3–13.4	10.5 ^c	8.1–17.5	11.7 ^d	536
Poland	2.2–21.0	6.0	4.2–20.9	11.3	381
U.S.	1.5–18.5	9.6	10.2–29.0	16.2	172
Russia ecosystems					
Meadow-bog	1.1–3.8	1.8	8.8–20.0	12.5	806
Forest-steppe	1.1–3.9	2.6	5.1–24	14.8	806
Forest	2.2–3.8	3.0	—	6.4	806

^a *Dactylis glomerata*.

^b *Trifolium repens*.

^c *Lolium perenne*.

^d *Trifolium pratense*.

TABLE 16.6
Copper in Food Plants Grown in Various Countries^a (mg/kg)

Plant	Range	Mean
Wheat, grains ^b	3.6–6.3	5.3
Wheat, grains ^c	1.3–10	4.7
Barley, grains	4–15	5.5
Rye, grain	—	4.5
Oats, grains	2–6	3.6
Cabbage	3–4	—
Lettuce	6–8	—
Carrot, roots	4–8.4	5.7
Onion, bulbs	4–6	4.9
Tomato, fruits	6–9	—
Potato, tubers	3–6.6	4.4
Tea, leaves ^d	—	20

^a Presented are common, possible background values from various sources, unless otherwise stated.

^b After Škrbić B. and Onjia A. (2007), for wheat from Serbia.

^c After Kumpulainen (1996) and Eriksson (2001), for wheat from seven countries.

^d After Wong et al. (1998), data for Kenya.

A number of projects have been carried out recently on Cu levels in edible plants, since about 30% of daily Cu intake by adults in Europe is from cereals and potatoes.¹²⁴⁷ Based on monitoring studies in Poland (7000 sample sites), the geometric mean concentrations of Cu were calculated (in mg/kg) for: cereal grain, 3.7; potatoes, 4.5; and grasses, 5.5.¹⁵¹⁴ These values are fairly similar to those presented for other countries (Tables 16.6). Wolnik et al.¹⁵⁴⁹ estimated, for the United States, mean content of Cu in potatoes as 0.96 mg/kg and in sweet corn 0.45 mg/kg. The recent reference for food compositions in the United States gives the following values for Cu in some categories of plant food (range, mg/kg FW): (1) vegetables: 0.1–3.2, celery root and garlic cloves, respectively; (2) fruits: 0.3–4.0, grapes and avocados, respectively; (3) cereals: 0.3–13.0, oats and rye, respectively; and (4) nuts: 0.2–23.8, fresh coconut meat and shelled Brazil nuts, respectively.¹²⁹¹

Most plants and bacteria have developed a resistance against Cu excess. Puig et al. (2007) described that small Cu-binding proteins play a protected function in Cu homeostasis. Some plants of the mint family (e.g., *Aeollanthus biformifolius* and *Becium homblei*) are good indicators of Cu deposits and, when grown on mineralized land, contain Cu at level of 13,700 and 1000 mg/kg, respectively (Hutchinson, 1979; Jenkins, 1980). Cu-tolerant plant communities and the role of Cu-hyperaccumulators in geochemical prospecting are described broadly by several authors (Kovalevsky,¹³⁷² Brooks,¹²⁴⁴ Vernadsky¹⁵³²).

Plants growing on Cu-polluted sites tend to accumulate increased amounts of this metal, especially near industrial areas, and in soils treated with Cu-bearing herbicides (Fishelson et al., 1994; Reimann et al., 1999). Thus, coffee trees from African plantations using Cu herbicides contain the following amounts of Cu (in mg/kg): bark, >1000; leaves 400; and roots 150 (Lepp and Dickinson, 1994). Forest trees, for example, pine trees, grown near a Cu-smelter in Finland contain also very high amounts of Cu (in mg/kg): bark, 1500; phloem, 66; wood, 11; and needles, 500 (Heliövaara and Väisänen, 1991).

Excess Cu in tropical plantations is of special concern. In plantations of citrus, coffee, cacao, tea, olives, and vineyards, Cu-fungicides have been applied for quite a long time. Now, microorganisms have developed a resistance to Cu, but the accumulation of this metal in surface soils is harmful to

TABLE 16.7
Copper Content of Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Part	Mean or Range of Content	Country	Reference
Metal processing industry	Lettuce, leaves	64	Australia	57
	Blueberry, leaves	75	Canada	866
	Grass, tops	21	Great Britain	1005
	Grass, tops	20–70 ^a	Canada	245
	Horsetail, tops	70–250 ^a	Canada	245
	Sugar beet, leaves	79–590	Poland	1161
	Dandelion, tops	73–274 ^b	Poland	380
	Dandelion, roots	22–199 ^b	Poland	380
	Wheat, grains	21	Poland	1006
Urban garden	Radish, roots	2–14	Great Britain	167
	Leafy vegetables	4–19	U.S.	628
Sludged or irrigated farmland	Grass, tops	14–38	Holland	297
	Rice, grains	4	Japan	395
	Rice, roots	560	Japan	395
	Potato, tubers	5	Germany	176
Fungicide treatment	Coffee ^c		Kenya	1058
	Medium roots	21.6		
	Fine roots	154.0		
	Trunk wood	6.7		
	Trunk bark	1122.5		
	Whole stems	9.4		
	Foliage	409.4		
	Beans	17.6		

^a For 1.6- to 5.8-km distance from a smelter.

^b For 0.5- to 2.5-km distance from a smelter.

^c 68-year-old coffee bushes, 236 mg/kg Cu in surface soil.

many new plant species. In old plantations, a significant increase in Cu content is noticed in consumed parts of plants. For example, tea leaves contain Cu from 20 mg/kg (Kenya) to about 80 mg/kg (Japan), of which up to 30% is easily extracted by hot water. The Cu concentrations in tea drinks are from 9 to 19/L.¹⁵⁵⁰

II SILVER

A INTRODUCTION

The geochemical characteristics of Ag are similar to those of Cu, but its concentration in the Earth's crust is about 1000 times lower than Cu and averages around 0.06 mg/kg (Table 3.2). In some sandstones and calcareous rocks its abundance can be enriched up to about 0.2 mg/kg (Table 16.2). After weathering it is relatively and easily precipitated in alkaline reduction-potential media and S-rich media.

The most common Ag minerals are: argentite, Ag₂S; cerargyrite, AgCl; arsenide, Ag₃As; pyrargyrite, Ag₃SbS₃; proustite, Ag₃AsS₃; and polybasite (Ag,Cu)₁₆Sb₂S₁₁. Ag is easily combined with minerals of other trace elements, such as Se, Te, As, Sb, and Bi (Etris, 1997). Minute

concentrations of Ag impurities occur often in sulfide minerals, for example: sphalerite, ZnS ; pyrite, FeS_2 ; chalcopyrite, CuFeS_2 ; and galena, PbS .

The global annual production of Ag in 2008 was estimated as 20.9 kt (USDI, 2009). The specific metallurgical processes applied to Ag-bearing minerals depend on whether the primary metal is Cu, Zn, Pb, or Au. However, most often it is recovered as byproducts at Cu and Zn ores exploration.

Silver was discovered about 4000 BC, when it was used as jewelry and a medium of exchange. Presently, the major part of the Ag production is used in the manufacturing and photographic industries. It can be recycled from spent photographic processing solutions, and photographic and x-ray films. Its demand is also in different other sectors, including: batteries, coins, jewelry, silverware, brazing and soldering, catalysts, and electronics.

B SOILS

The average Ag content for worldwide soils is estimated as 0.13 mg/kg, and range of its mean contents in soils of various countries is 0.05 and 0.13 mg/kg (Table 3.2). Smith and Carson⁷³⁹ have estimated soil Ag concentration to be between 0.03 and 0.09 mg/kg, whereas the background concentration of Ag, as reported by the US EPA (1981), range from 0.1 to 0.2 mg/kg.

The literature published on Ag distribution in the environment was reviewed by Smith and Carson⁷³⁹ and Mukherjee¹⁴³⁰ and shows the common range of Ag in soil to be 0.03 to 0.4 mg/kg. Ag in Canadian soils ranges from 0.2 to 3.2 mg/kg and for British standard soil samples Ag was reported to average 0.4 mg/kg.^{96,629,818} Recently calculated by Jones et al.,¹⁰⁴² the background Ag levels were <0.1 mg/kg, while soils contaminated by past mining activities in Wales contained up to 9 mg/kg Ag. Near Ag–Pb mining areas in the United Kingdom, soils contain this metal at the range of <0.1–18 mg/kg (Jones et al.¹⁰⁴³). Rasmussen et al. (2001) reported for garden soil and street dust in Canada contents of Ag at 0.4 and 0.2 mg/kg, respectively.

Data given by Shacklette and Boerngen⁷⁰⁶ show Ag in the plow zone of mineral soil to be 0.7 mg/kg, and in soils rich in OM, to be from 2 to 5 mg/kg. An average Ag content given for soils by Wedepohl⁸⁵⁵ ranges from 0.01 to 5 mg/kg, and values established by Bowen⁹⁴ range from 0.01 to 8 mg/kg. The Ag concentrations in soils of Poland do not exceed 1 mg/kg, with the exception of soils from the Cu smelter vicinity where the highest Ag content was 16 mg/kg.¹³⁹⁰ All higher values for Ag in soils are found in mineralized areas. Davies and Ginnever⁶⁸ found up to 44 mg/kg Ag in soils from the vicinity of old base metal mines, and Guseva¹³²¹ found up to 30 mg/kg in soils from Moscow surroundings. The EDTA-soluble Ag in Japanese soils ranges from 0.024 to 0.167 mg/kg, and in polluted soils is greater than 1.5 mg/kg.¹²⁰⁸ Kiriluk³⁹⁴ reported the range of Ag from 0.44 to 0.93 mg/kg in chernozems of vineyards.

Common species of Ag in soils are simple cations, Ag^+ , Ag^{2+} , and AgO^+ ; and complex anions that predominate in soil solution: AgCl_2^- , AgCl_3^{2-} , $\text{Ag}(\text{SO}_4)_2^{3-}$ (Kabata-Pendias and Sadurski, 2004). Despite several mobile complexes, Ag apparently is immobile in soils if the pH is above 4.

In soils, Ag is present primarily as sulfides associated with Fe, Pb. Also MnO_2 has a strong affinity for Ag, and appears to be the most significant sorbent of this metal.⁹⁴⁸ Ag may occur also as complex ions associated with chlorides and sulfates which are mostly insoluble or sparingly soluble (Cappel, 1997). Jones et al.^{1042a} described that the Ag behavior in soils is controlled mainly by pH–Eh conditions and OM. Humic substances are known to absorb and complex Ag. Sikora and Stevenson¹¹⁴⁸ studied the impact of organic substances on the availability of Ag. Maximum binding capacity of HA and FA ranges from 0.81 to 1.85 mM Ag/g at pH 6.5, and it is more closely related to the magnitude in N contents of humic substances than to acidic functional group contents. Jones and Peterson¹⁰⁴³ described that adsorption and retention of Ag by HA and FA in soils may limit its phytoavailability. Thus, the excess of Ag in soils of a low OM content is more phytotoxic than in soils of a high OM content. Ag_2S added to soils affected the growth reduction of meso and micro-biota (Ewell et al. *vide* Kabata-Pendias and Mukherjee, 2007). Ag ions have a great affinity for

binding sulfhydryl groups of some organic compounds. In general, the sorption of Ag by soil components is very strong, and nearly half of the total Ag is “residual” in immobile species.

C PLANTS

Concentrations of Ag in plants are reported by Smith and Carson⁷³⁹ to range from 0.03 to 0.5 mg/kg. Chapman¹³¹ established the intermediate range of Ag in plant foodstuffs as 0.07 to 2.0 mg/kg. The lowest concentrations of this metal (up to 0.0027 mg/kg) are reported for cereal grains (Table 16.8). Ag concentrations differ greatly between plant species and between times of sample collection. Horowitz et al.³²⁵ reported that Ag in plants sampled in September was much lower than in plants sampled in May. They found Ag in plants to range from 0.01 to 16 mg/kg, with the highest values being for fungi and green algae. Especially fungi and mushrooms from Ag-contaminated sites accumulate much Ag, up to 150 mg/kg (Table 16.8).

The amount of Ag absorbed by several plants (e.g., horsetail, lichens, mosses, fungi, and some deciduous trees) seems to be related to its contents of soils. Thus, Ag can be concentrated to toxic levels in plants growing in Ag-mineralized areas.^{120,417} Soil Ag is apparently deposited in root tissues in the form of Ag₂S and/or metallic, and therefore is excluded from metabolic processes. However, AgNO₃ can be easily taken up by plants, and is toxic in relatively low concentrations (<8.5 μM/L). AgNO₃ is reported to be the most toxic compound to terrestrial plants, of which the most sensitive are lettuce (NOEC at concentration 0.75 mg/L), and radish and corn (NOEC at concentration 7.5 mg/L).¹⁴⁶⁵

Wallace et al.⁸⁴¹ wrote that about 5 mg/kg Ag in the tops and about 1500 mg/kg in the roots of bush beans greatly reduced yields, but the plants grew without toxicity symptoms. Krizkova et al. (2008) exposed sunflower plants to high Ag concentrations (up to 1 μM/L) and observed significant decrease of plant growth and protein contents, whereas the activity of urease was markedly enhanced. Ozoliniya,¹¹⁰⁹ on the other hand, reported that Ag at 10 μg/L in the nutrient solution stimulated the growth of grass roots. This author speculated that some cations (e.g., Ag, Co, and Cu) can indirectly change cell metabolism, resulting in a higher growth rate of cells. As described by Hendrix and Higinbotham,³¹⁵ Ag can substitute for K⁺ sites in membranes and thus inhibit the absorption of other cations by roots.

TABLE 16.8
Silver in Plants and Fungi from Various Sites (mg/kg)

Plant	Range or Mean	Reference
Uncontaminated Sites		
Cereal grains	<0.0005–0.0027	Eriksson (2001)
Cereal products	0.008–0.14	Cunningham and Stroube (1987)
Vegetables	0.007–0.039	Cunningham and Stroube (1987)
Fruit	<0.05	Cunningham and Stroube (1987)
Grasses	0.06–5.04	Cunningham and Stroube (1987)
Ag-contaminated Sites		
Fungi (various) ^a	119	Eisler (1996)
Mushrooms ^b	120–150	Falandysz et al. (1994)

^a Vicinity of AgI-seeding generator site.

^b Soil with addition of Ag₂S.

Silver is very toxic to heterotrophic bacteria and thus is widely used as an aseptic substance. However, some bacteria (e.g., *Thiobacillus ferrooxidans*) are capable of accumulating great amounts of Ag.¹⁴³⁰ Ag compounds are known to precipitate bacterial proteins as well as to form insoluble complexes with ribonucleic acids.⁸⁵⁶

III GOLD

A INTRODUCTION

The abundance of Au in the continental crust averages 4 µg/kg (Table 3.2). Its concentrations in both sedimentary and igneous rocks vary from 0.5 to 6 µg/kg (Table 16.2).

Gold has a tendency to occur in the free state and tends to remain in this form due to its great chemical resistance. It occurs most commonly in the form of the native metal. Relatively common Au minerals are: calaverite, AuTe₂; montbrayite, Au₂Te₃; petzite, Au₃(AgTe)₂; and sylvanite, AuAgTe₄. It also may be a minor constituent of some types of ores. There are several oxidation states of Au (Table 16.1), however the occurrence of Au⁺, and Au³⁺ is most common in the environment.

The global Au production in 2008 was 2.33 kt (USDI, 2009). There are several Au-mining methods depending on type of deposits. Relatively common are flotation methods based on the amalgamation with Hg and bio-methods of dissolving Au from solution. Recently, Au became an important by-product from nonferrous Cu and Pb ores.

Gold is very resistance to oxidation and corrosion. It is widely used in jewelry, coinage, electroplating, electronics, dentistry, and as catalyst and antiarthritic drugs.

B SOILS

The average Au content of soils is estimated as 3 µg/kg and often is elevated in organic soils (Tables 3.2 and 16.2). Agricultural soils of Sweden contain Au at level <5 µg/kg (Eriksson, 2001). Some alluvial soils, soils with postmining Au deposits, and soils amended with Au-enriched sludge may contain much higher Au levels that are reported to range from 43 to 473 µg/kg (Williams et al.,¹⁵⁴⁴ McBride et al., 1997; Rashed and Awadallah, 1998). Lakin et al.⁴⁵³ described that in mineralized areas, Au in forest mull ranged from 0.05 to 5.0 mg/kg, while mineral fractions contained from 0.04 to 0.44 mg/kg. According to these authors, Au distribution in soil profiles depends on the origin of soil material and its weathering stage. It may be concentrated in fine soil particles or in cobbles and pebbles, and is most often enriched in the humus layer and bituminous OMS. However, distribution of Au within soil profiles may follow different trends, depending on its content in parent rocks and microorganisms activity. According to Lakin et al.⁴⁵³ the Au behavior in soils is highly controlled by OM.

In most soils, Au forms several complex ions such as AuCl₂²⁻, AuBr₄⁻, AuI₂⁻, Au(CN)₂⁻, Au(CNS)₄⁻, Au(Se₂O₃)₂³⁻ which are relatively mobile. Au complexes such as Au(OH)₃ · H₂O°, AuClOH⁻, and Au(OH)₂FA are known to be formed in tropical lateritic soils. Au seems to be transported most often in the form of organometallic compounds or chelates.⁹⁷ Thus, the chemistry of Au in soils is essentially a chemistry of complex compounds since no simple Au cations exist in soil solutions.⁴⁵³

Various bacteria and archaea, cyanobacteria in particular, control the Au solubilization and precipitation in auriferous and rhizosphere soils (Reith et al., 2007). There is also observed the Au mobilization in soils by cyanide released into soil solution by cyanogenic plants.⁴⁵³ Biologically mediated formation of calcretes and pedogenic carbonates is often associated with the Au coprecipitation (Mumm and Reith, 2007). Soil bacterial communities (e.g., *Bacillus cereus*) accumulate Au in spores up to 1100 µg/kg compared to a background of 2 µg/kg, and may be used for the exploration of Au deposits (Reith et al., 2005; Reith and Rogers, 2008). Reith and McPhail (2007) emphasized the role of microorganisms in the Au mobility in semi-arid and tropical regions.

In rain forest lateritic soils, Au complexes may be easily mobilized and thus readily available. In the Au mining area of Sri Lanka, high concentration of Au in peat and algal mats was increasing with depth and correlated with Fe, Mn, Co, Zr, Na, Mg, and K (Dissanayake and Kritsotakis, 1984).

The global balance of the Au accumulation in sewage streams is estimated at 360 t/year (Eisler, 2004). Sewage sludge may be a major source of Au when applied to soils. Elevated contents of Au have been reported as follows (in mg/kg):

- 0.18–2.35, soils at Au mining area in Australia (Lottemoser, 1995).
- 0.5–4.5, sewage sludge, Germany (Eisler, 2004).
- 0.5–3.0, sewage sludge, United States (Lottemoser, 1995).

Increased levels of Au in surroundings of some metal mining areas have been observed.

The Ni industry (on the Kola Peninsula) is, together with geogenic factors, a source of increased Au levels in O-horizon (Niskavaara et al., 2004).

C PLANTS

Plants can absorb Au in soluble forms, and when Au enters root vascular systems, may be easily transported to the tops. In reducing media, however, Au precipitates on the cell surface and thus inhibits membrane permeability.

Plants grown in uncontaminated sites usually contain Au in the range of 0.5–10 µg/kg (Table 16.9). Girling et al.²⁶³ gave the background Au content in vegetation as <1 µg/kg. In most cases, Au is concentrated more in roots than in above-ground parts. Also Greger¹³¹⁶ calculated that the Au content in the reference plant should be 1 µg/kg. Accumulator plants (e.g., *Artemisia persia*, *Prangos popularia*, *Stripa* sp.) may contain Au at levels of 0.1–100 mg/kg.

Root exudates of cyanogenic plants are known to dissolve Au. The ability of microorganisms to mobilize elemental Au was reported by some authors (Jones et al.,^{1042a} Borovička et al., 2005; Reith and Rogers, 2008). In most cases, microorganisms in the rhizosphere are responsible for the mobility and the phytoavailability of this metal (Eisler, 2004). However, this process is still not fully understood. The bioaccumulation of Au is also observed in stems and needles of Corsian pine tree (*Pinus laricio*) and in other plants growing in soils with Au levels of 1–25 mg/kg (Pyatt, 1999). Higher concentrations of Au in seeds than in leaves and stems were reported for planted fenugreek

TABLE 16.9
Gold in Plants Growing in Various Sites (µg/kg)

Plant, Site	Mean or Range	Reference
Various plants		Davies ¹²⁷²
Uncontaminated sites	<5.0	
Gold mining area	3–19	
Faba bean, contaminated sites		Rashed and Awadallah (1998)
Leaves	170	
Stems	50	
Pods	40	
Pericarp	36	
Testa, seeds, cotyledon	<7	
Mineralized areas		
Various plants	0.7–6.5	Girling et al. ²⁶³
Poplar, roots	2–28	Messerschmidt et al. (2000)

and lupin (both of *Leguminosae* family), whereas the highest Au content is reported for bean leaves (Table 16.9) According to Ozoliniya and Kiunke,⁵⁸⁸ Au in barley and flax is detectable only in roots, in the range of 14–22 µg/kg.

The Au concentration in plants and shrubs grown in various sites has been extensively used for the biogeochemical survey for Au mineralized areas, especially in Russia (Vernadsky¹⁴³²). Some plants (e.g., *Sedum acetatum*, *Phacelia sericea*, *Artemisia* sp.) were used successfully for the biogeochemical prospecting (Girling et al.²⁶³). Promising results were reported also for the use of Au hyperaccumulation for phytomining (Anderson et al., 1999). Various plant species collected from mineralized areas of British Columbia contained from 0.7 to 6.5 mg/kg Au, and the herbaceous plant *Phacelia sericea* (family *Hydrophyllaceae*) appeared to be the best Au accumulator.²⁶³ Horsetail is also known as a good indicator for Au; however, Cannon et al.¹²⁰ reported Au to be in the range of 0.1–0.5 mg/kg (AW) in horsetail species from Alaska, and only slightly higher Au concentrations were found in plant samples from mineralized areas. A broad range of Au, from 224 to 7450 mg/kg, was observed in lichens from the vicinity of an Au mine in New Zealand (Williams et al.¹⁵⁴⁴). Increased Au level in lichens is reported for vicinity of the Ni industry on Kola Peninsula (Niskavaara et al., 2004).

Several plant species are relatively resistant to higher Au concentrations in tissues. Au toxicity leads to necrosis and wilting by loss of turgidity in leaves.

Some microfungi (e.g., ectomycorrhizal and terrestrial saprobes) are reported to accumulate Au between 20 and 30 µg/kg (Borovička et al., 2005). According to these authors, Au levels in *Boletus edulis* (extomycorrhizal sp) may be up to 235 µg/kg. Increased Au concentrations in microfungi are controlled by several factors of which humidity and pH are of real importance.

17 Trace Elements of Group 12 (Previously of Group IIb)

The Group 12 consists of three metals: zinc (Zn), cadmium (Cd), and mercury (Hg). Their oxidation states usually are not higher than +2 (Table 17.1).

They all are relatively mobile in the Earth's surface and their cycling may be highly modified by the accumulation by plants and organic debris. These metals have comparatively high electronegativity values and easily form bonds with other elements, especially with S anions and with several organic compounds. Thus, they all are of great importance in the biochemistry. Although sulfides of Zn, Cd, and Hg are insoluble in water, compounds of Zn and Cd immediately hydrolyze, but the corresponding compounds of Hg are rather resistant to hydrolysis. The toxicity of Cd and Hg is well known, whereas Zn has enormous biological importance.

I ZINC

A INTRODUCTION

Average Zn content of the Earth's crust is estimated at 70 mg/kg, and the same average level is for the worldwide soils (Table 3.2). Zn is quite uniformly distributed in magmatic rocks, whereas in sedimentary rocks it is likely to be concentrated in argillaceous sediments, up to 120 mg/kg (Table 17.2). It is very mobile during weathering processes and its easily soluble compounds are readily precipitated by reactions with carbonates, or it is absorbed by minerals and organic compounds, especially in the presence of sulfur anions. Common Zn minerals are sphalerite, α -ZnS; wurzite, β -ZnS; zincite, ZnO; smithsonite, ZnCO_3 ; willemite, Zn_2SiO_4 ; and hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$. All these minerals contain about 50% of Zn.

Global production of Zn in 2008 was 11.3 Mt (USDI, 2009). The principal Zn ores are sphalerite, wurzite, and smithonite. Zinc ores contain trace metals, such as Pb, Cu, Ag, and Cd, of which Cd is most closely associated with Zn.

Zinc is used in many industries, mainly as corrosion protection of steel. It is an important component of various alloys and is widely used as catalyst in different chemical production (e.g., rubber, pigments, plastic, lubricants, and pesticides). It is also used in batteries, automobile equipment, pipes, and household devices. Its different compounds have dental and medical applications.

B SOILS

The general values for the average total Zn contents in soils of different groups, all over the world, range between 60 and 89 mg/kg (Table 3.2). Contents of Zn are closely associated with soil texture and usually are the lowest in light sandy soil. Its elevated concentration is often observed in calcareous and organic soils (Table 17.2).

Mean contents of Zn in soils reported for several European countries vary between 7 and 89 mg/kg, being the lowest for Denmark and the highest for Italy (Angelone and Bini, 1992; Kabata-Pendias and Pendias¹³⁵⁷). Median Zn value in sandstone soils of Brazil is 4 mg/kg, whereas in limestone soils it is 19 mg/kg (Melo et al., 2006). Range for Zn in soils of South Africa is given as 12–115 mg/kg, at established highest MTL value as 185 mg/kg (Herselman et al., 2005). Japanese agricultural soils contain Zn within the range of mean values from 59 to 99 mg/kg, with the lowest

TABLE 17.1
Selected Properties of Trace Elements of Group 12

Element	Atomic Number	Atomic Mass	Atomic ^a Radius (pm)	Density (20°C, g/cm ³)	Valence ^b
Zn, zinc	30	65.38	153	7.13	+2
Cd, cadmium	48	112.41	171	8.65	+2
Hg, mercury	80	200.59	176	13.55	+1, +2, +3

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation state.

value for sandy Acrisols and the highest for Andosols (Takeda et al., 2004). Zn contents in agricultural soils of Sweden range from 6 to 152 mg/kg, with mean value of 65 mg/kg (Eriksson, 2001). In the United States, the geometric mean of Zn in cultivated soils was reported to be 43 mg/kg, in the range of <3–264 mg/kg (Holmgren et al.¹³²⁹). Zn in agricultural soils of Vietnam (Red River Delta) ranges from 25.6 to 236.8 mg/kg (Ho and Egashira, 2007). Relatively high Zn contents, up to 14,925 mg/kg (at average 61 mg/kg), are reported for some top soils of the Slovak Republic (Čurlík and Šefčík, 1999).

Agricultural practices are known to increase Zn contents of surface soils. However, data presented by Huang and Jin (2008) show rather small variation in Zn contents of soils under different use pattern: from 57 to 82 mg/kg, in soil from the grain crop field and soil from the greenhouse vegetable field, respectively. The Zn balance in surface soils of different ecosystems shows that the atmospheric input of this metal exceeds its output due to both leaching and the production of biomass (Table 3.13). Only in unpolluted forest regions of Sweden the discharge of Zn by water flux is reported to be higher than its atmospheric input.⁸¹⁶

TABLE 17.2
Abundance of Trace Elements of Group 12 in Rocks and Sils (mg/kg)

Rock/Soil	Zn	Cd	Hg
Earth's crust	52–80	0.1–02	0.02–0.09
Igneous rocks	—	—	—
Ultramafic	40–60	0.03–0.05	—
Mafic	80–120	0.13–0.22	0.004–0.01
Acid	40–100	0.05–0.2	0.03–0.08
Sedimentary rocks	—	—	—
Argillaceous	80–120	0.2–0.3	0.2–0.4
Sandstones	15–30	<0.04–0.05	0.01–0.05
Calcareous	10–25	0.04–0.1	0.02–0.05
Soils ^a	70 ^b	0.41 ^b	0.07 ^b
Arenosols (sandy)	31–61	0.01–0.2	0.08–0.7
Podzols (medium loamy)	47–63	0.08–0.3	0.01–1.2
Cambisols (heavy loamy)	35–75	0.2–0.5	0.02–1.5
Calcisols (calcareous)	50–100	0.4–0.8	0.01–0.5
Histosols (organic)	57–100	0.2–2.5	0.04–1.12

^a Soil groups are given according to the WBR (Table 3.1).

^b World soil average (Table 3.2).

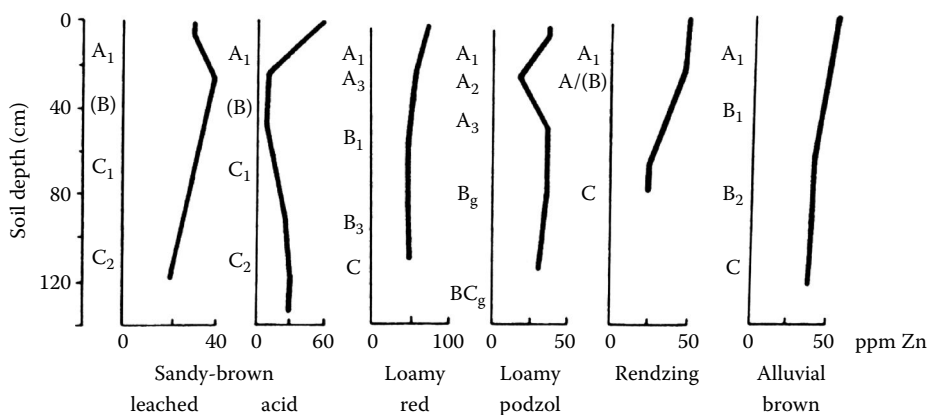


FIGURE 17.1 Distribution of Zn in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

Regularity in the large-scale Zn occurrence in soils indicates that parent material, soil formation processes, and OM govern the initial Zn status in soils. The clay fraction, especially when composed of vermiculite and gibbsite, contributes significantly to the Zn content of soils (Vega et al., 2007). Sorption of Zn onto clay lattice is stronger than that of Cd (Antonladis and Tsadilas, 2007). The sorption capacity of SOM resulted in Zn accumulation in the surface horizons of most soils (Figure 17.1).

The most common and mobile Zn in soil is believed to be in forms of free and complex ions in soil solutions, but several other ionic species that occur as nonspecifically and specifically adsorbed cations can also be easily mobilized in soils (Figure 17.2). Important factors controlling the mobility of Zn in soils are very similar to those listed for Cu, but Zn appears to occur in more readily soluble forms. Many studies of Zn adsorption and retention in soils were reviewed by Lindsay.⁴⁷⁶ Smolders and Degryse (2006) discussed Zn fixation processes in soils. According to these authors, Zn fixation is relatively slow and highly controlled by soil pH and forms of metal added. However, aging of these reactions affects in the increased pool of fixed Zn with time. Results of studies on Zn adsorption on TiO_2 indicated that under increased temperature Zn became more mobile, which might be related also to other sorption processes (Li et al., 2008b).

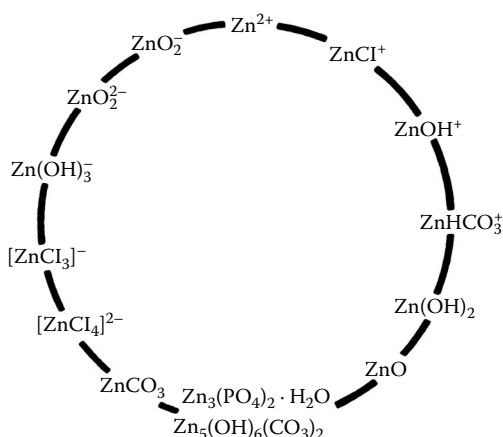


FIGURE 17.2 Ionic species and compounds of Zn occurring in soils.

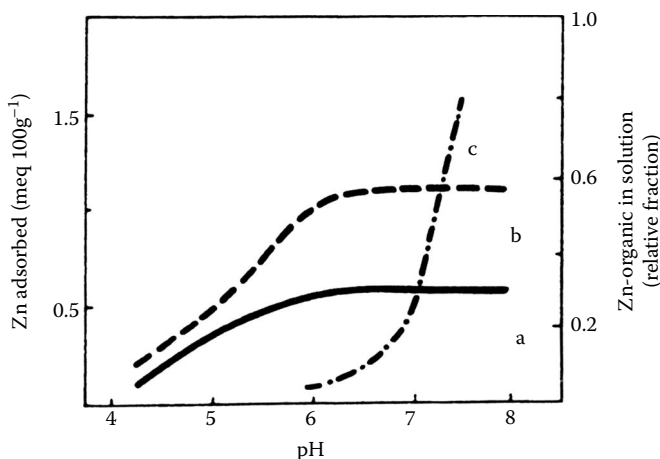


FIGURE 17.3 Influence of soil pH on adsorption of Zn at (a) 20 mg/kg and (b) 40 mg/kg Zn levels in initial solutions and on formation of soluble Zn–organic complexes in the solution of loamy silt soil (c). (From McBride M. B. Blasiak J. J., *Soil Sci. Soc. Am. J.*, 43, 866, 1979. With permission.)

Although Zn is very mobile in most soils, clay fractions and SOM are capable of holding Zn quite strongly, especially at neutral and alkaline pH regimes (Peganova and Edler, 2004). However, DOM is an important factor affecting Zn mobility in soils with alkaline pH range of 7–7.5 (Wong et al., 2007).

The immobilization of Zn in soils is highly controlled by phosphorous and clays (Kumpiene et al., 2008). Kabata-Pendias and Krakowiak¹³⁵⁵ calculated that the clay fraction controls up to about 60% of Zn in soils (Figure 17.3). Apparently, there are two different mechanisms of Zn sorption: one in acid media related to cation exchange sites, and the other in alkaline media that is considered to be the chemisorption and is highly influenced by organic ligands. Moreover, oxides and hydroxides of Al, Fe, and Mn appear to be of importance in binding Zn in some soils. Especially goethite (αFeOOH) reveals a great affinity to Zn sorption. Microorganisms reduce this process due to the accumulation of metal in living cells (Perelomov and Kandeler, 2006).

McBride and Blasiak⁵¹⁹ stated that nucleation of Zn hydroxide on clay surfaces might produce the strongly pH-dependent retention of Zn in soils (Figure 17.2). The adsorption of Zn^{2+} can be reduced at lower pH (<7) by competing cations, and this results in easy mobilization and leaching of Zn from light acid soils (Table 3.13). At higher pH values, although an increase of organic compounds in soil solution becomes more evident, Zn–organic complexes may also account for the solubility of this metal (Figure 17.4). In sandy acid soils, on the contrary, OM seems to be the most important soil component for binding Zn, whereas oxides (hydro) of Al, Fe, and Mn appear to be of minor importance. As Zyrin et al.⁹¹¹ reported, Zn in soils is associated mainly with hydrous Fe and Al oxides (14–38% of total Zn) and with clay minerals (24–63%), whereas its readily mobile fractions and its organic complexes make 1–20% and 1.5–2.3%, respectively.

Abd-Elfattah and Wada² found the highest selective adsorption of Zn by Fe oxides, halloysite, allophane, and imogolite and the lowest by montmorillonite. Thus, clay minerals, hydrous oxides, and pH are likely to be the most important factors controlling Zn solubility in soils, whereas organic complexing and precipitation of Zn as hydroxide, carbonate, and sulfide compounds appear to be of much lesser importance. Zn can also enter some layer lattice silicate structures (e.g., montmorillonite) and become very immobile.

SOM is known to be capable of bonding Zn in stable forms; therefore, the Zn accumulation in organic soil horizons and in some peat is observed. However, stability constants of Zn–OM in soils are relatively low, although a high proportion of Zn is bound to OM in mineral soils. According to

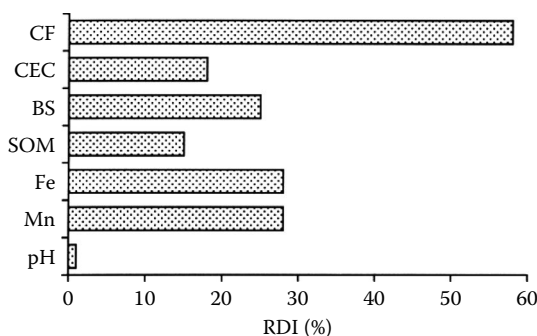


FIGURE 17.4 Relative explanation index (RDI) of statistically significant relationship between Zn and soil parameters in mineral soils at the 99% confidence level ($N=5780$). Soil parameters: CF, clay fraction <0.02 mm; CEC, cation exchange capacity; BS, base saturation; SOM, soil organic matter; Fe, total content; Mn, total content; pH, in water (soil:water ratio, 1:2.5).

Prusty et al. (2008), elevated Zn contents in wetland (96.1 mg/kg) than in woodland (30.8 mg/kg) is due to higher SOM contents in the wetland. The addition of sewage sludge to soils modifies the distribution pattern of Zn, significantly increasing contents of two Zn species, easily soluble and exchangeable (Figure 17.5). Wada and Abd-Elfattah⁸³⁴ gave the range in maximum Zn adsorption by different soils as 16–70 meq/g for Ca-saturated samples. This finding supports several statements about Ca-exchange sites with a high selectivity for Zn. Shukla et al.⁷²¹ reported that the order of Zn adsorption in different cation-saturated soil was the following: $H < Ca < Mg < K < Na$.

In soil solution, Zn occurs in forms of free and complexed ions, as cations: Zn^{2+} , $ZnCl^+$, $ZnOH^+$, $ZnHCO_3^+$, and as anions: ZnO_2^{2-} , $Zn(OH)_3^-$, $ZnCl_3^-$ (Kabata-Pendias and Sadurski, 2004). Zn-organic species may also occur in the solution. According to Tyler and Olsson (2002), the concentration of Zn in cultivated soil solution was 78 (12–223) $\mu\text{g/L}$, whereas in natural soil it was 35 (13–72) $\mu\text{g/g}$. However, depending on the techniques used for obtaining soil solution, its concentrations vary between 21 and 570 $\mu\text{g/L}$.¹³⁵⁷ Itoh et al.³⁴¹ reported a maximum Zn in solution as 17,000 mg/L and this value is, apparently, for highly contaminated soils. In very acidic soils ($\text{pH} < 4$), Zn concentration in solutions was reported to average 7137 mg/L. The Zn concentration in soil solutions of Podzols in Taiga (Russia) varies from 20 to 350 mg/L and is higher in the upper layer.¹⁴²⁶ Although Zn is highly soluble in solution of peaty soils, it occurs mainly in colloidal forms (up to 60% of total content). Zn anionic organic and inorganic complexes account for up to 40%, whereas cationic

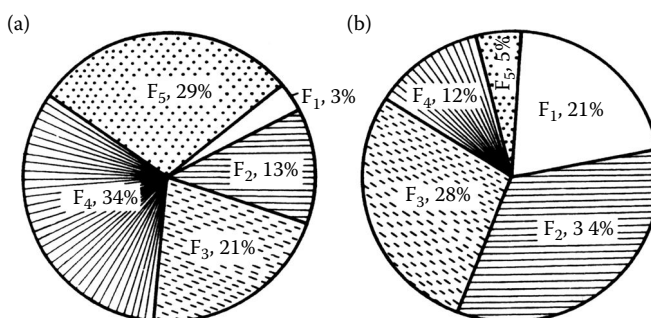


FIGURE 17.5 Variation in Zn species in soils under sludge application: (a) unsludged soil, (b) sludged soil. Zn species: (F₁) easily soluble; (F₂) exchangeable; (F₃) associated with hydrous oxides; (F₄) bound to organic matter; and (F₅) residual. (From Dudka S., Chlopek A., *Water Air Soil Pollut.*, 51, 153, 1990. With permission.)

forms are present only below 10%.¹⁴²⁷ Shi et al. (2005) studied the kinetics of Zn release from soils and concluded that desorption is the main process contributing metal to the solution. Meers et al. (2006) reported, however, that pH is a key factor in determining Zn solubility, and thus, its concentration in soil solution.

Zinc is most readily mobile and available in acid light mineral soils. As Norrish⁵⁷⁰ stated, the Zn fractions associated with the Fe and Mn oxides are likely to be the most available to plants. Acid leaching is very active in the Zn mobilization; thus, losses of this metal are observed in certain horizons, particularly of podzols and brown acid soils derived from sands.

The immobilization of Zn in soils rich in Ca and P, in well-aerated soils with S compounds, and in soils containing enhanced amounts of certain Ca-saturated minerals such as allophane, imogolite, and montmorillonite, as well as hydrous oxides, has an important practical impact on the Zn deficiency of plants. Zn deficiencies most frequently result from management practices used during crop production (e.g., overliming, P fertilization, and OM amendment).

1 Contamination of Soils

The anthropogenic sources of Zn are related, first of all, to the nonferrous metal industry, and then to agricultural practice. Contemporarily observed soil contamination with Zn has already brought Zn to an extremely high accumulation in top soils in certain areas (Table 17.3). Additional problems related to Zn pollution are changes in the metal speciation. For example, in soil (loamy sand, pH 6.1, OM 1.25%) amended with Zn-enriched sewage sludge, an increase of easily available Zn species was observed from 3% to 21%, and weakly bound or exchangeable Zn species from 21% to 34% of the total Zn content (Figure 17.5). It is rather very difficult to estimate Zn pollution in soils. Diatta et al. (2008) proposed (after Müller) to use the Zn geoaccumulation index that helps to assess Zn contamination of soils.

In places closer to nonferrous smelters and contaminated sites, the levels of Zn along with other metals might be quite high, that is, from 443 to 1112 mg/kg (ATSDR, 1994). High levels of Zn in soils around mining areas were reported by Angelone and Bini (1992) for different countries, as follows (in mg/kg): the Netherlands, 1020; Austria, 8900; and Greece, 10547. Soils surrounding a Zn smelter in Poland contain this metal within the range of 202–4832 mg/kg, at an average of 1062 mg/kg (Diatta et al., 2008). Elevated Zn content of natural source (from bauxite parent material), at the range of 126–683 mg/kg, is reported for Oxisols in Jamaica (Davies et al., 2003).

TABLE 17.3
Zinc Contamination of Surface Soils (mg/kg)

Site and Pollution Source	Country	Mean or Range	Reference
Old mining area	Great Britain	220–66,400	808, 915
	Great Britain	455–810	165
Nonferrous metal mining	Great Britain	185–4500	165, 786, 1005
	U.S.	500–80,000	615, 1108
	Russia	400–4245	467, 567
Metal-processing industry	Canada	185–1397	363
	Belgium	66–180,000	1142
	Holland	915–3626	305
	Greece	550–16,000	559
	Japan	132–5400	891, 403, 926
	Poland	1665–13,800	224, 1015, 1526
	U.S.	155–12,400	365, 259
	Romania	3000	1126
	Zambia	180–3500	573

According to Voegelin et al. (2008), the Zn speciation in contaminated soils is highly controlled by pH and Zn content. In acidic soils, Zn was mainly found in mobile fractions (extraction: NH_4NO_3), whereas in neutral soils it was mainly in the mobilizable fraction (extraction: NH_4 -acetate). In soils heavily polluted with Zn, the formation of Zn-pyromorphite, $\text{Zn}_5(\text{PO}_4)_3\text{OH}$, was observed, mainly at the surface of grass roots, which suggests the impact of the rhizosphere on this process.¹²⁶³

The fate of the Zn from various sources (e.g., atmospheric deposition, fertilizers, pesticides, sewage sludge, and ashes) differs depending upon its chemical species and their affinity to soil parameters. Variability in Zn isotopes is suggested to be amenable to identify different atmospheric zinc sources, however, under consideration of its biochemical cycling within the peat profiles (Weiss et al., 2007).

According to data presented in the *Etat de l'Environnement Wallon* (1995), Zn contents in fertilizers and slurry are as follows (in mg/kg):

- Triple superphosphate, 142–625
- NPK fertilizers, 61–200
- Ammonitrate fertilizers, <2
- Pig slurry, 919
- Cow slurry, 580
- Poultry slurry, 495

In the EC Report (2003), the average concentration of Zn in sludge of the EU countries was reported as 811 mg/kg. The lowest concentration of Zn in sludge, analyzed in year 2000, was reported for the Netherlands (131 mg/kg) and the highest for Portugal (1670 mg/kg). Zinc loads, with various materials used for soil amendments, vary in the following order (in g/ha): compost, 1190; pig manure (solid), 1080; and triple superphosphate, 54 (Döhler et al., 2002). The MAC values for Zn (in kg/ha/year) vary from 30 (EU countries) to 140 (United States). In most ecosystems, the anthropogenic source of Zn might highly influence its elevated contents, especially in surface soils. The Zn balance in crop-farm soils vary (in g/ha/year) from –115 in Germany to 838 in France (Eckel et al., 2005).

Calculation of the first half-life of Zn in contaminated soils in lysimeters showed that Zn decrease was relatively rapid and that soil containing 2210 mg/kg Zn will reduce Zn content by half during 70–81 years.³⁹⁵ These results, however, were reported for paddy soils with a long drainage period. Based on the results of other experiments, the half-life of Zn as a pollutant in soil may be much longer. Amelioration of Zn-contaminated soils is commonly based on controlling its availability by addition of lime or OM or both.

C PLANTS

1 Absorption and Transport

Soluble forms of Zn are readily available to plants, and the uptake of Zn has been reported to be linear with metal concentration in the nutrient solution and in soils (Figure 17.6). The rate of Zn absorption differs greatly among both plant species and growth media. The composition of the nutrient solution, particularly the presence of Ca, is of great importance (Figure 17.7). At a high pH value (7.2–7.8), Zn uptake by barley is also closely correlated with its content in soils (Figure 17.8).

Disagreement exists in the literature whether Zn uptake is an active or a passive process. Moore,⁵⁴⁸ Loneragan,⁴⁸⁹ and Hewitt³¹⁷ reviewed this topic, and it may be summed up that several controversial results strongly suggest that Zn uptake is mostly metabolically controlled; however, it can also be a nonmetabolic process. Fusuo Zhang et al.^{1004a} reported that root exudates of Zn-deficient cereal plants were active in mobilizing both Zn and Fe from various precipitations in soils. The Zn distribution in plant parts usually follows the pattern: roots > foliage > branch > trunk. Small lateral roots retain more Zn than other vegetation components. The form in which Zn is absorbed by roots

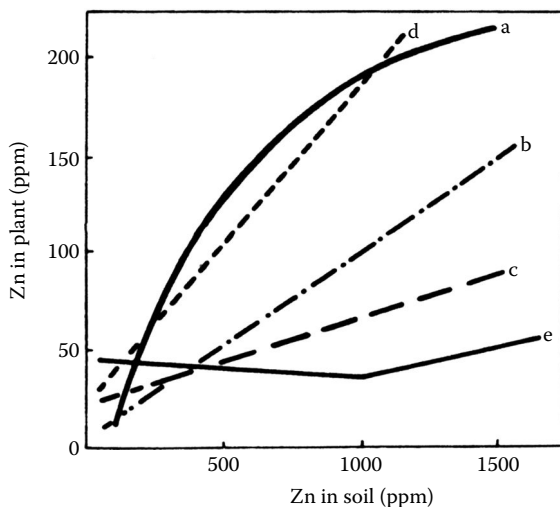


FIGURE 17.6 Zn uptake by plants from soil contaminated by this metal. (a) Pasture herbage, (b) wheat straw, (c) wheat grains, (d) potato stalks, and (e) potato tubers.^{176,783}

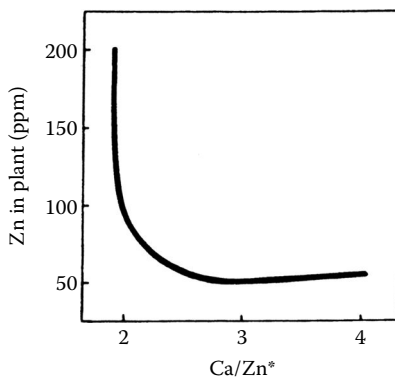


FIGURE 17.7 Zn content of cereal tops at the boot stage as a function of Ca/Zn ratio in the soil solution. Note: *Ca/Zn ratio is given in powers of ten. (From Abrahams P. W., Thornton I., *Trans. Inst. Min. Metall. Sect. B.*, 96, 1, 1987. With permission.)

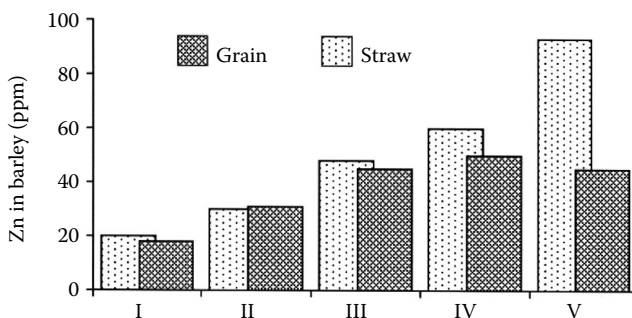


FIGURE 17.8 Impact of Zn added, as Zn and Pb smelter flue-dust, to the soil on concentration of Zn in spring barley grain and straw. Zn levels in soils (mg/kg): I, 60 (blank); II, 560; III, 960; IV, 4060; V, 15,060. (Adapted from Kabata-Pendias, A. and Pendias, H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 400, 1999 (Po).)

has not been precisely defined. There is, however, general agreement on the predominating uptake of both hydrated Zn and Zn^{2+} . Several other complex ions and Zn-organic chelates may also be absorbed.^{489,788,856} Von Wiren et al. (1996) studied Zn^{2+} -phytometallophore complexes and observed that these complexes were readily absorbed by maize roots. Baize and Tomassone (2003) proposed a model for Zn transfer from soils into wheat grains, based on the extractions with DTPA and NO_3NH_4 . Wolterbeek and van der Meer (2002) studied, using radionuclide, transport rates of metals in a plant, and observed the highest mobility of Zn as compared with As, Cd, and Cu.

Several findings support the general statement that Zn is generally bound to soluble low-molecular-weight proteins; however, the formation of Zn-phytate and other insoluble Zn complexes was also reported by Weinberg⁸⁵⁶ and Tinker.⁷⁹⁸ Zn is reported to be concentrated in chloroplasts, especially in those of some plants (e.g., spinach). This metal is also likely to be accumulated in vacuole fluids and in cell membranes.⁷⁹⁸ Fractions of Zn bound to light organic compounds in xylem fluids and in other plant tissue extracts may suggest its high mobility in plants.^{789,822} According to Tinker,⁷⁹⁸ the portion of Zn bound in complexes with a negative charge constitutes more than half of the total metal present in plants.

Some authors regard Zn as highly mobile, whereas others consider Zn to have intermediate mobility. Indeed, when given abundant supplies of Zn, several plant species have mobilized appreciable quantities of this metal from old leaves to generative organs; but, when under Zn-deficiency conditions, the same species have mobilized little, if any, Zn from old leaves. Hence, in summary of several findings, it may be stated that Zn is likely to be concentrated in mature leaves. However, Scheffer et al.^{688a} reported the highest Zn content of barley leaves, sheaths, and internodes to always be during the phase of intensive growth, which demonstrated a great Zn fluctuation within the plant during the vegetative period. On the contrary, Ylärinta et al.⁸⁹⁵ observed a small variation in the Zn content of wheat during the whole growth period.

2 Biochemical Functions

Zinc plays essential metabolic roles in plants, of which the most significant is its activity as a component of a variety of enzymes, such as dehydrogenases, proteinases, peptidases, and phosphohydrolases. Lindsay,⁴⁷⁶ Price et al.,⁶³⁰ and Shkolnik⁷¹⁸ indicated that the basic Zn functions in plants are related to the metabolism of carbohydrates, proteins, and phosphates, and also to auxins, RNA, and ribosome formations. There is an evidence that Zn influences the permeability of membranes and that stabilizes cellular components and systems of microorganisms.^{718,856} Zn is believed to stimulate the resistance of plants to dry and hot weather and also to bacterial and fungal diseases. This may be due to positive Zn effects on levels of proteins and chlorophyll and abscisic acid, as observed in bean seedlings (Zengin, 2006).

Plant species and varieties differ widely in their susceptibility to Zn deficiencies. Although these deficiencies are relatively common (Table 5.7), their diagnosis is rather complex, and the best diagnoses are obtained when based on visual symptoms, plant analyses, and soil testing together. It must be emphasized, however, that for certain crops and soils, two chelating extractants, DTPA and EDTA, give linear relationships between Zn in plants and the soluble Zn pool in the soils.^{476,797}

Nambiar and Motiramani⁵⁶⁰ reported that Zn levels in tissues used for the prediction of its deficiency often fail as the diagnostic test and that tissue Fe-to-Zn ratios appear to be more promising for the prediction, even of hidden Zn deficiency. The critical Fe-to-Zn ratio in maize was found to be about 6.0. Lindsay⁴⁷⁶ extensively reviewed patterns of Zn deficiency and its common occurrence throughout the world, and listed the most important factors contributing to the Zn deficiency as follows:

- Low soil Zn content
- Calcareous soils and pH above 7
- Soils low in OM
- Microbial inactivation of Zn in soil

- Limited Zn uptake by roots due to restricted root zone and to cool spring seasons
- Differential responses of plant species and genotypes
- Antagonistic effects

The Zn toxicity and tolerance in plants have recently been of special concern because the prolonged use of Zn fertilizers, as well as its input from industrial pollution, is reflected in enhanced Zn content of surface soils. Several plant species and genotypes are known to have a great tolerance to Zn and a great selectivity in absorbing Zn from soils. Plants usually reflect changes on the Zn content of growth media and therefore are good indicators in biogeochemical investigations. Some genotypes grown in Zn-rich soils or in areas of heavy atmospheric Zn deposition may accumulate extremely large amounts of this metal without showing symptoms of toxicity. Petrunina⁶¹³ and Kovalevskiy⁴¹⁷ listed several species, particularly of the families *Caryophyllaceae*, *Cyperaceae*, and *Plumbaginaceae*, and also some trees, as extremely good Zn indicators that concentrate this metal in the range from about 0.1 to about 3% (Table 5.9). Tolerant species may reduce the effect of excessive Zn concentrations either by metabolic adaptation and complexing or by limiting the metal presence at cellular locations or by immobilization in storage tissues. According to Wani et al. (2007), bioinoculants are effective in the attenuation of Zn toxicity in plants and thus may be useful in remediation of contaminated sites.

Most plant species and genotypes have great tolerance to excessive amounts of Zn. Chlorosis, mainly in new leaves, and depressed plant growth are the common symptoms of Zn toxicity (Table 5.8). An excess of Zn can be bound by phytic acid in roots of some crop plants (e.g., soybean, tomato, cabbage, and wheat). This mechanism does not work, however, when there is also an excess of Cd.¹⁵⁰⁷ Białońska et al. (2007) reported that bilberry leaves (*Vaccinium myrtillus* L.) produce more phenolic compounds that might have a protective function against the Zn (and possible other metals) toxicity.

Zinc phytotoxicity is reported relatively often, especially for acid and heavily sludged soils. The physiology and biochemistry of the toxic effects of Zn in plants are likely to be similar to those reported for other trace metals; however, Zn is not considered to be highly phytotoxic. The toxicity limit for Zn depends on plant species and genotypes, as well as on a growth stage. Hence, Zn content at about 300 mg/kg is reported to be toxic to young barley, whereas about 400 mg/kg is toxic to oats at the beginning of tillering.^{171,322} However, in root tissues, where Zn is immobilized in cell walls or complexed in nondiffusible Zn proteins, critical concentrations of Zn are much higher. Sensitive plant species are reported to be retarded in growth when their tissues contain 150–200 mg/kg Zn.¹⁰⁵² Most commonly, however, the upper toxic levels range in various plants from 100 to 500 mg/kg.¹⁰⁸¹

Some species, such as *Thlaspi caerulenscens* and *Thlaspi ochroleucum*, are known to hyperaccumulate Zn, and are recommended for *in situ* decontamination of soils. The first species of *Thlaspi* appears to be more resistant to a very high concentration of Zn and to significantly higher accumulated amounts of Zn (up to 8000 mg/kg) than the second species (up to 2000 mg/kg). Both plants, however, accumulate more Zn in shoots than in roots.¹⁴⁰⁹ Mean extraction of Zn by these plants from soils contaminated with Zn (124–444 mg/kg Zn) was calculated as 14–57 kg/ha.¹⁴⁰⁷

The deficient content of Zn in plants is established as 10–20 mg/kg (Table 5.4). These values, however, may vary considerably because the Zn deficiency reflects both the requirements of genotypes and effects of the interactions of Zn with other elements within the plant tissues. Zn is not translocated readily in plants; deficiency occurs generally first in younger leaves. Owing to Zn deficiency, some plants remain short and underdeveloped, which is the result of an inadequate supply of the growth hormone, indole acetic acid. Large crop losses were cited owing to Zn deficiencies, for example, for citrus orchards in California, peach trees in Texas, and for various crops in Australia. Yazdi and Khorsandi (2008) described the positive effects of Zn fertilization on yield and phytoestrogen contents of pomegranates (*Punica granatum* L.) grown in calcareous soils of arid regions.

3 Interactions with Other Elements

Zinc is relatively active in biochemical processes and is known to be involved in several biological and chemical interactions with several elements. Findings of Graham et al.¹⁰¹³ supported earlier reports of Loneragan et al.¹⁰⁷⁴ that the Zn deficiency interferes with the control of ion absorption, causing ions to accumulate to high levels in plant tissues. Thus, supplying Zn is expected to decrease the uptake of most nutrients. This was not observed for Fe, whereas the uptake of B and Mn was especially depressed. Graham et al.¹⁰¹³ were the first to report that inadequate Zn content leads to increased uptake of B and S by barley.

Zn–Cd interactions appear to be somewhat controversial, since there are reports of both antagonism and synergism between the two elements in the uptake–transport processes. Nan et al. (2002) concluded that Cd–Zn interaction is synergistic under field condition, thus increasing both metals in soils affect their increase accumulation in plants. Kitagishi and Yamane³⁹⁵ explained the observed synergism in rice plants in terms of Zn competition for the Cd sites, resulting in an increase in Cd solubility, and in Cd translocation from roots to tops. Wallace et al.⁸⁴⁶ reported a high Cd accumulation in roots of plants at a high Zn level and at a low pH of the solution. Earlier findings, well illustrated by those of Lagerwerff and Biersdorff,⁴⁴⁹ however, show antagonism between these cations in the uptake–transport process. It may be stated that the ratio of Cd to Zn in plant media controls the occurrence of synergism and antagonism between these cations. Papoyan et al. (2007) observed that high Zn concentrations in *Thlaspi caerulescens* increased Cd tolerance and Cd levels of a plant.

Zn–Cu antagonistic interactions were observed, in which the uptake of one element was competitively inhibited by the other. This might indicate the same carrier sites in absorption mechanisms of both metals.

Zn–Fe antagonism is widely known and its mechanism is apparently similar to the depressing effects of other trace metals on the Fe uptake. An excess of Zn leads to a marked reduction in Fe concentration in plants. Olsen⁵⁸¹ stated that Zn interfered more with the absorption and translocation of Fe than it did with Cu and Mn. There are two possible mechanisms of this interaction—the competition between Zn^{2+} and Fe^{2+} in uptake processes, and the interference in chelation processes during the uptake and translocation of Fe from the roots to tops. In addition, Fe decreases the Zn absorption and toxicity. Observed Zn–Fe synergism is reported to be linked with the P supply. It is suggested that at a relatively high accumulation of P and Zn in roots, the precipitation of FePO_4 in root tissues can account for the increase in Fe uptake.¹⁰¹³

Zn–As interaction was reported by Shkolnik⁷¹⁸ as a possible antagonism observed in decreases of toxic effects of As excesses after Zn treatments. Similar interaction between Zn and Hg was also mentioned, although not described clearly.

Zn–P interaction is widely observed and reported for many crops, especially after phosphate and lime applications.⁴⁹¹ Norvell et al.¹¹⁰⁴ studied Zn–P interaction in alkaline soils and stated that the specific effects of P on the concentration of Zn^{2+} in soil solution were small and observed only when the Zn^{2+} content was raised previously by Zn fertilizers. However, the addition of P also caused small decreases in concentrations of other divalent cations. The P–Zn imbalance, resulting from excessive P accumulation, is known to induce Zn deficiency. This antagonism appears to be based to a large extent on chemical reactions in root media.^{581,675} However, Smilde et al.⁷³⁸ stated that Zn–P antagonism could not be explained by only mutual immobilization and that this interaction is mainly a plant physiological characteristic. Usually, the antagonistic effect of P on Zn concentration was more pronounced than that of Zn on P. The optimum P:Zn ratio for corn plants is 100. At lower and higher values, a steep decrease in yield was observed.^{1542a} A balanced P and Zn nutrition was reported by Shukla and Yadav⁷²² to be essential for the proper activity of *Rhizobium* and N fixation.

Zn–N interaction is mostly a secondary “dilution” effect due to the increase of biomass because of the heavy N treatment. Olsen⁵⁸¹ reported an enhancement of Zn in tops due to a higher bonding of Zn by proteins and amino acids in root tissues.

Zn–Ca and Zn–Mg interactions vary for a given plant and media (Table 5.11). Apparently, several other factors, pH in particular, control the antagonistic and synergistic character of interactions between these elements. Olsen⁵⁸¹ stated that reactions, which lowered Zn deficiency by Mg applications, occurred within the plant rather than within the soil, but a competition between Mg and Zn in soil-exchange sites cannot be precluded.

4 Concentrations in Plants

Zinc contents of plants vary considerably, reflecting the different factors of various ecosystems and of the genotypes. However, its concentrations in some plants, cereal grains, and pasture herbage from different countries do not differ widely. Mean values for Zn in cereal grains range from 24 to 33 mg/kg, in wheat and oats, respectively (Table 17.4), and did not show any clear differences between countries. The median Zn content ($N = 5128$) of wheat grains from France is 15.5 mg/kg (range 7–43 mg/kg).¹²¹³ Wheat grains ($N = 14$) from Serbia contain Zn within the range of 26.6–44.3 mg/kg, at the average value of 3.2 mg/kg (Škrbić and Onjia, 2007).

The reference for food compositions in the United States (Ensminger et al.¹²⁹¹) gives the following values for Zn in some categories of food plants (mg/kg FW): (1) vegetables: range 0.7–8.0, the lowest value for celery root, and the highest for spinach; (2) fruits: range 0.4–3.0, the lowest value for grapes, and the highest for black currant (European); (3) cereals: range 0.7–32.5, the lowest value for barley pearls (cooked), the highest for rye (whole grain); and (4) nuts: range 5–42.3, the lowest value for coconut (meat, fresh), and the highest for Brazil nuts (shelled). Chinese tea leaves contain Zn from 26 to 40 mg/kg, of which up to 50% is extracted by hot water. Tea drinks have from 0.08 to 0.17 ng Zn/L.¹⁵⁵⁰

Background content of Zn in grass and clover throughout the world is relatively stable, and its mean levels in grasses range from 12 to 47 mg/kg, and in clovers range from 24 to 45 mg/kg (Table 17.5).

TABLE 17.4
Zinc Content of Food Plants (mg/kg)

Plant	Range	Mean
Wheat, grains	23–37	24
Barley, grains	20–30	26
Oats, grains	29–37	33
Rye, grains	29–31	28
Rice, grains	1–41	18
Sweet corn, grains	25–36	—
Bean, pods	32–38	—
Cabbage, leaves	24–31	27
Lettuce	44–73	—
Carrot, roots	21–27	24
Beet, roots	28–46	—
Onion, bulbs	22–32	25
Potato, tubers	10–26	17
Tomato, fruits	17–26	—
Apple, fruits ^b	—	1.2
Banana, fruits ^b	—	2.8

^a Presented are common, possible background, values from various sources, unless otherwise indicated.

^b Peganova and Eder, 2004.

TABLE 17.5
Mean Levels and Ranges of Zinc in Grass and Clover of Immature Growth from Different Countries (mg/kg)

Country	Grasses		Clovers		Reference
	Range	Mean	Range	Mean	
Bulgaria	24–50	34	—	—	680
Czech Republic	15–35	25 ^a	—	—	154
Germany	15–80	47 ^a	20–50	24 ^b	65
Germany	27–67	31 ^c	—	—	596
Finland	28–39	32	—	—	388
Great Britain	22–54	33	—	—	165
Hungary	21–36	27	30–126	39	803
Japan	18–38	28	23–55	34	770
New Zealand	16–45	28	20–49	27	536
Poland	12–72	30 ^d	16–86	37 ^e	838, 1045
Russia	—	—	—	45	501
Yugoslavia	6–11	—	48–94	62	623, 755

^a Mean value calculated from the given range.

^b Alfalfa.

^c Perennial rye grass and clover mixture.

^d Orchard grass.

^e White clover.

Environmental Zn pollution greatly influences concentrations of this metal in plants (Table 17.6). In ecosystems where Zn is an airborne pollutant, the tops of plants are likely to concentrate elevated amounts of Zn, up to about 0.1%. However, plants grown in Zn-contaminated soils accumulate a great proportion of the metal in roots. Flue dust is a source of easily available Zn to corn plants, independently of soil pH (Dos Santos et al., 2006).

II CADMIUM

A INTRODUCTION

The average Cd content for the Earth's crust is given as 0.1 mg/kg (Table 3.2). Its abundance is fairly similar in both igneous and sedimentary rocks (Table 17.2). The metal occurs rarely in nature in a pure form. Its common minerals are greenockite, CdS; octavite, CdSe; and monteponite, CdO. Cd is associated with Zn and Pb ore deposits, and its host minerals are sphalerite, biotite, amphiboles, and smithsonite, in particular.

Cadmium and Zn have similar ionic structures, electronegativities, and chemical properties (Table 17.1). However, Cd has a stronger affinity for S than Zn, and thus its mobility in an acidic environment is higher than that of Zn (Alloway, 1995). Although Cd has the same valence and similar ionic radius as Ca, it does not substitute for Ca in minerals. During weathering processes, Cd forms simple compounds, such as CdO, Cd(OH)₂, CdCl₂, and CdF₂ that are easily mobile and follow Zn, especially in sedimentation processes. Cd compounds are known to be isotypic with corresponding compounds of cations such as Zn²⁺, Co²⁺, Ni²⁺, Fe²⁺, Mg²⁺, and, in some cases, of Ca²⁺.

Cadmium is considered as being one of the most ecotoxic metals that exhibit adverse effects on all biological processes of humans, animals, and plants. This metal reveals its great adverse potential to affect the environment and the quality of food.

TABLE 17.6
Excessive Levels of Zinc in Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Part	Mean or Range	Country	Reference
Old mining area	Grass	65–350	Great Britain	165, 167
	Clover	450	Great Britain	513
Nonferrous metal mining	Onion bulbs	39–710	Great Britain	169a
	Lettuce	55–530	Great Britain	169a
Metal industry	Lettuce	316	Australia	57
	Chinese cabbage leaves	1300	Japan	403
	Oat grains	132–194	Poland	224
	Potato tubers	74–80	Poland	224
	Lettuce	213–393	Poland	224
	Carrot roots	201–458	Poland	224
	Blueberry tops	130–680	Poland	922
Urban garden	Radish roots	27–708	Great Britain	166, 167
	Leafy vegetables	35–470	U.S.	628
Sludged, irrigated, or fertilized farmland	Grass	126–280	Holland	297
	Sudan grass	66–250	Hungary	1177
	Rice grains	21	Japan	395
	Rice roots	4510	Japan	395
	Oat grains	27–85	U.S.	726
	Soybean leaves	156	U.S.	126
	Soybean seed	114	U.S.	126
	Sagebrush	2600 ^a	U.S.	278
	Potato tubers	36	Germany	176

^a AW basis.

The global production of Cd increased from 16.8 kt in 2003 to 20.8 kt in 2008 (USDI, 2009; WMSY, 2004). It is produced mainly as a by-product in mining and refining of Zn ores. Therefore, its supply is more dependent on the Zn production than on the Cd demand. Generally, 3 kg of Cd is produced from one ton of the Zn production. Cd is also recovered from recycled materials such as Zn–Cd batteries.

The main use of Cd is in the sector of Ni–Cd and Ag–Cd battery production. Relatively high amounts of Cd are used as pigments (yellow) and for coatings and stabilizers. Due to its unique physical and chemical properties, this metal is also added to alloys and used as stabilizers for various plastics.

B SOILS

The world average soil Cd concentration is estimated as 0.41 mg/kg. The main factor determining Cd contents of soils is parent material. The average contents of Cd in soils lie between 0.2 and 1.1 mg/kg (Table 3.2). In uncontaminated soils, its contents are highly governed by soil texture and range from 0.01 to 0.3 mg/kg in sandy soils and from 0.2 to 0.8 mg/kg in loamy soils (Table 17.2). Apparently, all values higher than background contents reflect the anthropogenic impact on the Cd status in top soils. Surface soils from major agricultural production areas of the United States contain Cd within the range of <0.01 to 2.0 mg/kg Cd (geometric mean, 0.175).¹³²⁹ Govindaraju¹³¹³ reported Cd contents in reference soils from different countries to range from 0.06 to 4.3 mg/kg.

Soils from Sichote-Alin (remote region of Russia) contain Cd from 0.2 to 1.14 mg/kg, with the greatest concentration in flooded soils.¹⁴²⁸ Relatively high Cd contents, up to 8.9 mg/kg (at average 0.3 mg/kg), are reported for some top soils of the Slovak Republic (Čurlík and Šefčík, 1999).

During weathering, Cd goes readily into mobile pool, and may form several types of complex ions and organic chelates. Its concentrations in soil solution vary, partly depending on techniques used for obtaining solution, from 0.2 to 300 µg/L. It may occur as cationic species: CdCl^+ , CdOH^+ , CdHCO_3^+ , CdHS^+ , and as anionic species: CdCl_3^- , Cd(OH)_3^- , Cd(OH)_4^{2-} , Cd(HS)_4^{2-} (Kabata-Pendias and Sadurski, 2004). Sposito and Page¹¹⁵⁵ predicted, based on a model, following species of Cd in soil solution: (1) in oxic soil, Cd^{2+} , CdSO_4^0 , and CdCl^+ ; (2) in acid soil, Cd, CdCl^+ , CdSO_4^0 ; and (3) in alkaline soil, CdHCO_3^+ . According to Taylor and Percival (2001), between 55% and 90% of Cd in soil solution is present as free metal ion Cd^{2+} and is readily available to plants. Welch and Norvell (1999) reported that, in addition to inorganic species, Cd in the soil solution occurs in complexes with various organic acids (e.g., amino acids, HA, and FA). Although the importance of SOM in the Cd fixation is proofed, a simple correlation analysis indicated that the metal mobility is significantly correlated mainly with pH (Basta et al., 2001). Mensah et al. (2008) used the WHAM VI for the prediction of Cd concentration in soil solution as a function of moisture content. The model resulted in $\text{RMSE}_{\log[\text{Cd}]} = 0.25$.

Smolders and Dedgryse (2006) reviewed different techniques used to measure labile and fixed pools of Cd and stated that more than half of the Cd content is in labile form in both soils with background content of Cd and soils amended with Cd. There is observed a slow immobilization of Cd in soil. The mobility and plant availability of Cd in wetland soil differ from that of upland soils. The metal is strongly retained in wetland soils, whereas it is available to plants under upland conditions (Grambrell, 1994). Land use and especially afforestation of agricultural soils have a significant impact on Cd speciation and thus, its mobility (Mäkelä-Kurtto et al., 2008).

Cadmium concentration in soil solution is relatively low and is reported to range from 0.2 to 6 mg/L. The much higher value (300 mg/L) reported by Itoh and Yumura³⁴² presumably indicates contaminated soil and corresponds to the value (400 mg/L) given by Kabata-Pendias and Gondek³⁷⁹ for contaminated soil. The solubility of Cd is closely related to the acidity of the soil solution (Figure 3.4). The critical acidity in mineral soils is within the pH range of 4.0–4.5, at which a drop in pH of merely 0.2 units results in a 3–5 times increase in Cd labile pool.⁹³⁸

Soil texture is an important factor governing Cd contents of soils. This relationship is well illustrated by the Cd geometric mean contents increasing with the content of the soil clay fraction. Light sandy soils of Poland contain 0.22 mg/kg Cd, whereas light loamy soils contain 0.31, and heavy loamy soils contain 0.51 mg/kg (Table 4.1). However, clay fraction is not a major soil factor controlling the Cd distribution; it contributes up to 10% of all relationships (Figure 17.9). A stronger

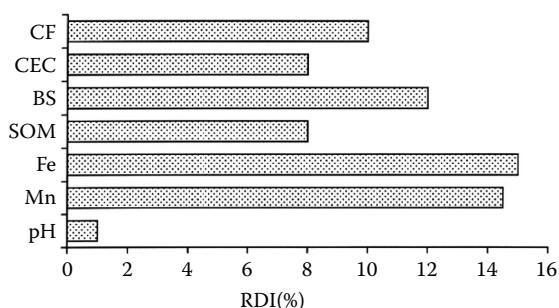


FIGURE 17.9 Relative explanation index (RDI) of statistically significant relationship between Cd and soil parameters in mineral soils at the 99% confidence level ($N = 5780$). Soil parameters: CF, clay fraction <0.02 mm; CEC, cation exchange capacity; BS, base saturation; SOM, soil organic matter; Fe, total content; Mn, total content; pH, in water; soil:water ratio, 1:2.5.

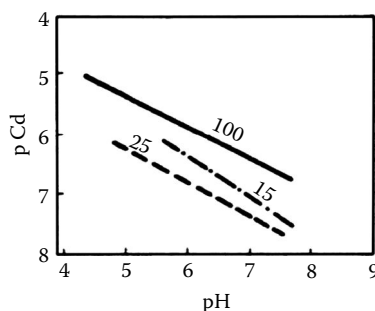


FIGURE 17.10 Solubility of Cd^{2+} in soils as a function of soil pH. Equilibration with 15, 25, and 100 mg Cd per 2 g of soil. (From Soon Y. K., *J. Sol Sci.*, 32, 85, 1981. With permission).

relationship is observed for Cd with Fe and Mn contents of soil; apparently, the oxides of these metals are of importance in soil at low pH (<5.5). Nevertheless, there is an opinion that Cd adsorption by clays is the predominant process that control the fixation of Cd (Farrah and Pickering,²²⁸ Tiller et al.,⁷⁹⁶ Soon⁷⁴⁷).

The pH-solubility diagram (Figure 17.10) indicates that above pH 7.5, Cd absorbed in soils is not easily mobile; therefore, the solubility of CdCO_3 , and possibly of $\text{Cd}_3(\text{PO}_4)_2$, would control the Cd mobility in alkaline soils. The adsorption capacity of hydroapatite for Cd decreases in the presence of other metals (Cu, Zn, Pb), due to the competitive metal sorption (Corami et al., 2008). There are several evidences that Eh-pH controls the Cd mobility in soils. Increasing pH results in increased sorption of Cd by SOM. Under conditions of a strong oxidation, Cd is likely to occur in the forms of CdO and CdCO_3 , and is likely to be fixed by phosphates. Matusik et al. (2008) reported that various Cd-phosphate compounds are formed depending mainly on soils' pH. Under anaerobic conditions, the Cd in soil solution is governed by sulfide precipitation (Christensen and Huang, 1999). Martin-Garin et al. (2002) reported that Cd mobility and sorption is controlled by calcite.

As John³⁶¹ reported, the coefficient of bonding energy of the Cd adsorption was higher for organic matter than for soil clays. Abd-Elfattah and Wada², on the contrary, stated that Fe oxides, allophane, and imogolite reveal the highest affinity for the selective adsorption of Cd. Hydroxides appear to be of minor importance in soil at low pH (<5.5). Grafe et al. (2007) suggested that Cd outer sphere complexes on kaolinite are mainly due to hindered Cd sorption to the Al octahedral sheets.

Results of several studies (Gadde and Laitien,²⁵³ Forbes et al.,²⁴⁰ Lamy et al., 1993) on Cd fixation by SOM and Fe/Mn hydroxides lead to some generalizations: (1) in all soil, Cd activity is strongly affected by pH, (2) in acid soils, the SOM and sesquioxides may largely control labile pool of Cd, (3) in alkaline soil, precipitation of Cd compounds is likely to account for Cd equilibria.

Low-molecular-weight OM fractions bound more Cd than do higher-weight fractions, whose affects increased the Cd mobility (Mahara et al., 2007). Karlsson et al. (2007) indicated that the role of carboxylate in Cd binding in organic soils increases as thiole groups become saturated.

Soil microbial activity is believed to play a significant role in the Cd behavior in soils. Chammugathas and Bollag⁹⁶² observed both binding of Cd and its subsequent release from soils under the influence of soil microorganisms. The tolerance and reaction of different microorganisms to increased Cd levels differ showing either increase or decrease of the indicator PLFAs (Shentu et al., 2008). Some microorganisms (e.g., *Actinomycete* R27) reveal a capability to accumulate increased level of Cd, may contain up to 1120 mg/kg (Ledin et al., 1999). Thus, remediation technique based on inoculating soils with microorganisms has been recently proposed for Cd-contaminated soils (Burd et al., 2000).

Isenbeck et al.¹⁰³³ reported that high carbonate concentration in soil solution leads to the total Cd precipitation and that no other soil factors are so active in the Cd immobilization. The rate and

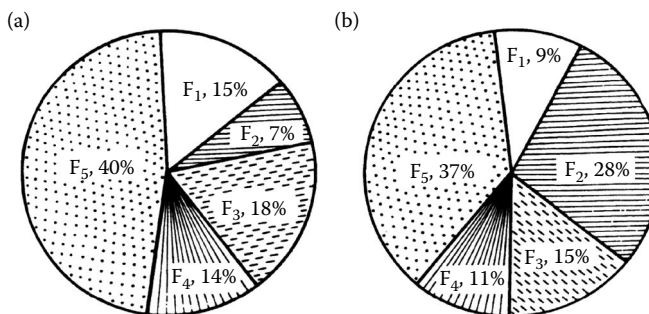


FIGURE 17.11 Variation in Cd species in soils under sludge application: (a) unsludged soil, (b) sludged soil. Cd species: (F₁) easily soluble; (F₂) exchangeable; (F₃) associated with hydrous oxides; (F₄) bound to organic matter; and (F₅) residual. (From Dudka S., Chlopecka A., *Water Air Soil Pollut.*, 51, 153, 1990. With permission.)

degree of these processes depend upon soil parameters of which the Eh–pH system is of a greater importance. This observation is also supported by findings of Fic⁹⁹² and Christensen.⁹⁶⁷

The Cd amounts bound to SOM and in residual fraction seem to be relatively stable in soil, whereas its exchangeable forms increase significantly under sludge application (Figure 17.11). Cd is the most mobile in acidic soils within the range of pH 4.55.5, whereas in alkaline soil Cd is rather immobile. However, as the pH is increased in the alkaline range, monovalent hydroxy ion species are likely to occur (e.g., CdOH⁺), which could not easily occupy the sites on cationic exchange complexes. The sorption of Cd is known to be a fast process. Christensen⁹⁶⁷ found that 95% of the Cd sorption takes place within 10 min, reaching equilibrium in 1 h and that the soil has very high affinity for Cd at pH 6. In the pH interval from 4 to 7.7, the sorption capacity of the soil increases approximately 3 times for a pH increase of one unit. On the contrary, Butt et al. (2008) reported that Cd in Australian krasnozems is slightly available to plant due to its high sorption (on average, 89% of total content) by amorphous metal oxides and SOM or on some silicates. Furthermore, McLaughlin et al. (2006) observed a lower Cd bioavailability (transfer to grain) from soils with biosolids than from soils with soluble Cd salt addition, possible due to interactions with Zn and dissolved OM present in biosolid.

Asami⁹²⁴ found that a half or more of the total Cd in paddy soils is readily extractable by 0.05 M CaCl₂. Lodenius¹⁰⁷¹ studied the mobilization of Cd in sand and peat soils under leaching with artificial acid rain (pH 3.6 and 5.4) and with salt solution (pH 7.0). In each case, the strongest leaching was achieved by a neutral solution containing Ca²⁺, K⁺, NO₃⁻, and SO₄²⁻ ions. This supports Laxen's conclusion¹⁰⁵⁷ that as alkalinity increases, Cd adsorption decreases, probably due to the competition from Ca²⁺ and Mg²⁺ ions. These findings have important implications for the development of realistic reclamation techniques for the management of Cd-enriched soils.

1 Contamination of Soils

In soils developed under the influence of humid climate, migration of Cd down the profile is more likely to occur than its accumulation in the surface horizon, thus the enrichment in Cd content observed so commonly in top soils should be related to contamination effects.

Soil contamination with Cd is believed to be the most serious health risk. Under man-induced conditions, Cd is likely to build up in surface soils (Tables 3.14 and 17.7). However, elevated levels of Cd in soils can also be of lithogenic (geogenic) origin. This is reported by Čurlik and Forgáč¹²⁶⁷ for alluvial soils derived from pyritized quartzes and from hydrothermally altered pyritized andezine in Slovakia, in which a high concentration of Cd up to 222 mg/kg is observed at a depth of 100–120 cm. This phenomenon is due to the redeposition of sulfide materials, which absorb some metals mobilized during weathering. Natural Cd anomalies have also been detected by Baize et al.¹²¹⁴ in

TABLE 17.7
Cadmium Contamination of Surface Soils (mg/kg)

Site and Pollution Source	Maximum or Range	Country	Reference
Mineralized bedrock and mining area	0.6–468	Great Britain	166, 808, 915
	2–336 ^a	Great Britain	959
	2–144	Belgium	728
Metal-processing industry	3.2–1781	Belgium	1142
	2–5	Bulgaria	611
	2–36	Canada	363
	9–33	Holland	305
	1.8–88	Japan	336, 403, 891, 926
	6–270	Poland	224, 871, 1015
	12	Romania	1126
	26–1500	U.S.	233, 1108
	0.6–46	Zambia	573
	1–17	Great Britain	959
Urban gardens	0.08–61	Poland	159, 1173
	0.02–13.6	U.S.	127, 628
	10–100 ^b	U.S.	1073
	3.9	Germany	1046
	7.3–8.1	Canada	243
Sludged, irrigated, or fertilized farmland	1.5–167	Great Britain	959, 987
	15–57 ^c	Holland	314
	2.5–5.6	Hungary	1177
	2.2–7.5 ^d	Japan	924
	0.4–107	Poland	1173
	2.6–8.3	U.S.	964, 1186
	1–10	U.S.	705a

^a Zn mining area.

^b Soils sludged since 1964.

^c 6 and 16 t dry matter sludge/ha/year, for 5 years.

^d Paddy soils.

France. These Cd-enriched soils are derived from Jurassic or Cretaceous limestone. The Cd contents of Jurassic rocks range broadly from 0.02 to 8.15 mg/kg. Elevated Cd level, at the range of 14–192 mg/kg, of natural sources (from bauxite parent material) is also reported for Oxisols in Jamaica (Davies et al., 2003).

The Cd concentration in top soils is reported to be very high in the vicinities of Pb and Zn mines and, in particular, smelting operations (Table 17.7). Sewage sludge and phosphate fertilizers are also known as important sources of Cd, and there are several comprehensive reviews of this subject (Fleischer et al.,²³³ Williams and David,^{878,879} Street et al.,⁷⁶¹ Chaney and Hornick,¹²⁹ von Jung et al.,³⁷² Smolders and Degryse, 2006). Poelstra et al.¹¹²¹ calculated the accumulation of Cd in soils due to the application of sewage sludge. The permissible level of Cd (i.e., 22 kg/ha) from this source will be reached, in different periods, depending upon soil variables and, in particular, upon the adsorption coefficient. The significant increase of weakly bound and exchangeable species of Cd in the sludged soils will affect its phytoavailability (Figure 17.11). Jones et al.¹⁰⁴⁴ gave an excellent example for the long-term increase of Cd in the soil plow layer in the Rothamsted Experimental Station, England (Figure 17.4). Both the Cd atmospheric deposition and fertilizers (farmyard manure or phosphate fertilizers) resulted in Cd increases. Changes in soil Cd levels in untreated plots were

from 0.51 to 0.77 mg/kg over a period of about 40 years. Even in the forests of remote regions in various countries, with the exception of one site in Sweden, the atmospheric input of Cd exceeded the output of this metal from the soil profile (Table 3.12). In France, some highly polluted soils are reported to contain over 100 mg/kg of Cd.¹²¹⁴

Industrial Cd emission is well documented as its significant source in agricultural lands of several countries. The highest Cd concentrations (in mg/kg) are reported for soils in the vicinity of metal-processing industries, for example, in Belgium, 1781; in Poland, 270; and in the United States, 1500 (Kabata-Pendias and Pendias¹³⁵⁷).

The deposition rate of Cd in Europe was established as 3.0 g/ha/year (Pacyna *vide* Kabata-Pendias and Mukherjee, 2007), whereas the smallest deposition rate 0.15 g/ha/year is reported for Finland (MAF, 1997). In Sweden, the wet deposition was calculated as 0.39 g/ha/year (Eriksson, 2001). In the United States, about 300 t of Cd (22% of the total release) was deposited on soils in 1996 (TRI96, 1998). The Cd balance in crop-farm soils vary (in g/ha/year) from—0.3 in Denmark to 4.4 in France (Eckel et al., 2005). In recent years, a decrease of Cd emissions from anthropogenic sources has been noted in some countries. For example, in Finland, the Cd emission decreased from 6.3 t in 1990 to 1.1 t in 1997.¹⁴³³ In Switzerland, Cd concentration in top soils decreased from 25.2 mg/kg in 1975 to 1.7 mg/kg in 1999 (Herter and Kuelling, 2001), whereas in the EU countries, it has decreased from 9 mg/kg in 1982/83 to 1.6 mg/kg in 1996/97 (Genderbien et al., 1999).

Major sources of Cd in soils is the atmospheric deposition, mainly from metal smelters (up to 1000 g/ha/year), and P fertilizers (up to 150 g/ha/year) (Alloway and Steinnes, 1999). P fertilizers are a continuous source of Cd in soils. The highest content of Cd (>100 mg/kg) is reported to be in raw phosphates from the United States (Idaho), and the lowest (<3 mg/kg) in phosphate rocks of igneous origin mined in Russia (Kola mine) and in Finland (Siilinjärvi).¹⁴²⁰ P fertilizers marketed in Brazil contain Cd within the range from <3 to 43 mg/kg (Bizarro et al., 2008).

Gunnarson¹³²⁰ reported the increasing addition of Cd to soils in Sweden since 1901 (Figure 17.12). Other data^{1044,1257} also show a significant increase of Cd concentration in agricultural soils (Figure 17.13). Increasing soil Cd is also reported by Sillanpää and Jansson¹⁴⁹¹ for the worldwide soils. The Cd contents of soils and of crop plants increased from 0.04 to 0.1 mg/kg and from 0.04 to 0.12 mg/kg, respectively, with increasing fertilization from 5 to 70 kg P/ha. The prediction presented by Stigliani¹⁵⁰⁸ indicates that due to the continuous increase of Cd in soils and decrease of soil pH, the transfer of Cd to the food chain will grow significantly with time. In the year 2010, the crop from acid soils (pH 5.0) can increase the PTWI doses up to 1200 mg Cd, which is several times higher than the dose accepted as the health-related limit for Cd intake by humans.

Cadmium concentration in P fertilizers is controlled by its contents in phosphorites (Table 4.4). Addition of P fertilizers is known to immobilize Cd soils (Hettiarachchi et al.¹³²⁸); however, there

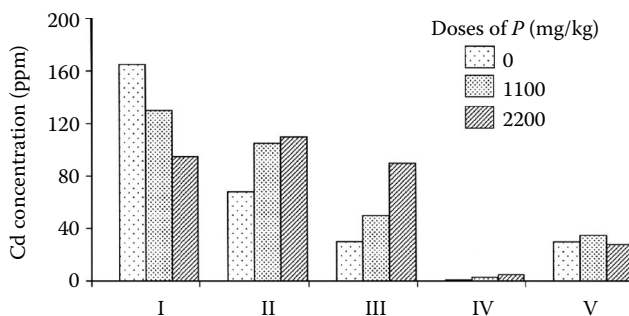


FIGURE 17.12 Influence of KH_2PO_4 on Cd fractionation in soil contaminated with Cd (370 mg/kg), soil pH 7.0 after CaCO_3 amendment. Fractions of Cd. (After Tessier, A., Campbell, P. G. C., and Bisson, M., *Analyt. Chem.*, 51, 844, 1979); I, exchangeable; II, carbonate; III, oxide; IV, organic; V, residual. (From Hettiarachchi, G. M., et al., *Proc. 4th Intern. Conf. Biogeochem. Trace Elements*, Berkeley, CA, June 23–27, 1997, 463. With permission.)

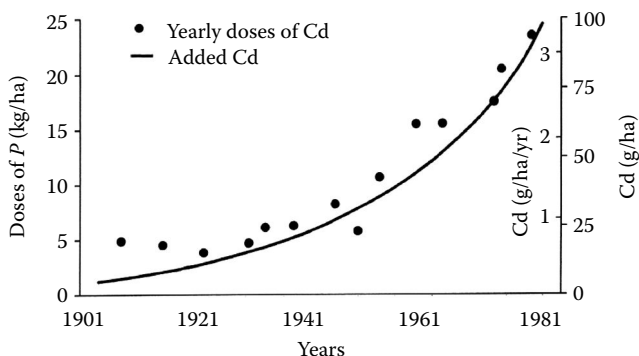


FIGURE 17.13 Cd input in Swedish agricultural soils with phosphate fertilizers. (Modified from Gunnarsson O., The relative role of fertilizers for the cadmium levels in the food chain under Swedish circumstances, *Cadmium Seminar*, Rosslyn, VA, November 20–21, 1980.)

are evidences that not all Cd can be fixed (Smolders and Degryse, 2006). The exchangeable fraction of Cd decreases with the presence of phosphate in soils, whereas carbonate and oxide fractions increase its mobility (Figure 17.14). On the contrary, Escrig and Morell¹²⁹⁵ reported that a tenfold increase in Ca concentration in soil reduced the Cd adsorption capacity by approximately 3 times.

Elevated Cd in soils decreases activities of urease and phosphatase. These effects are decreased when butachlor (herbicide) is added (Wang et al., 2007). The addition of rhamnolipid biosurfactant (biofugicide) mobilizes Cd, and the recovery of metal decreases with soil sorption capacity (Asci et al., 2008).

Because of the environmental significance of the Cd accumulation in soil, several techniques for the management of Cd-enriched cropland were investigated. Similarly, as in the case of Zn-contaminated soils, these techniques are based on increasing soil pH and CEC. Although liming generally is expected to decrease Cd absorption by raising the soil pH, it is not effective for all soils and plants. The maximum permissible rate of Cd addition to soil should depend strongly on the soil pH.

Several methods, including incineration of soils, adsorption and desorption processes, solubility, chemical treatment, and natural attenuation have been applied for the remediation of soils contaminated with trace metals (Rulkens and Honders, 1996; Cunningham and Berit, 2000; Hamon et al., 2006).

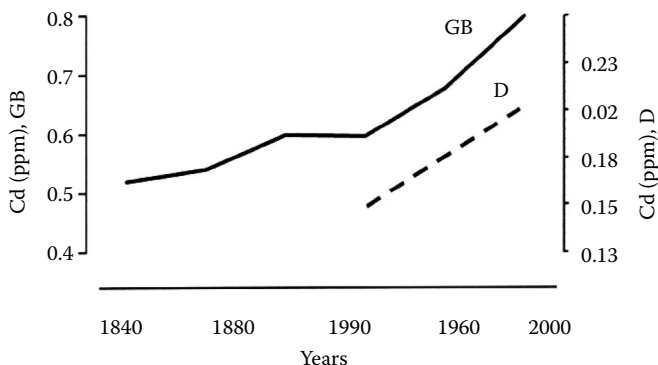


FIGURE 17.14 Changes in soil Cd levels in unfertilized plots of long-term experiments in Great Britain (GB) and Denmark (D). (Modified from Jones K. C., Symon C. J., Johnston A. E., *Trace Subst. Environ. Health*, Vol. 21, University of Missouri, Columbia, MO, 450, 1987; Christensen T. H., Tjell J. Chr., *Heavy Metals in the Environment*, CEP Consl., Edinburgh, U.K., 1, 40, 1991).

Liming is an old practice that reduces uptake of Cd, as well as other metals by crop plants. The effectiveness of liming on its adsorption by plants depends greatly on the relative change in pH and Ca^{2+} concentration in soil solution. Even coal fly ash (if it has alkaline properties) may decrease the Cd availability to plants. However, it may also be a source of Cd in soils. Kitagishi and Yamane³⁹⁵ reported that the best and most reliable results in reducing Cd availability was the layering of unpolluted soil over polluted soil to a depth of 30 cm.

In recent years, the phytoremediation technique has been applied on Cd (and other metals) contaminated soils (Dickinson and Pulford, 2005; Chaney et al., 1998). When plants are watered with ethylenediaminetetraacetic acid (EDTA), the uptake of trace metals from contaminated soils may be increased (Jørgensen, 1993). Although many soil parameters control Cd uptake by plants, some plants species reveal an unusual ability to its uptake and transfer to upper parts. Some plants proposed for the soil phytoremediation are *Alyssum murale*, *Thlaspi vaerulescens*, *Nicotiana tabacum*, *Zea mais*, *Salix viminalis*, *Helianthus annuus*, and *Viola baoshanensis*. Sugarcane also displays a tolerance to elevated Cd content in nutrient solution, with no symptoms of toxicity at Cd concentration 451 mg/kg in shoots. According to Sereno et al. (2007), sugarcane can be a potential candidate for the phytoremediation of Cd-contaminated soil. The crucial parameter in phytoextraction of trace metals are BCF and PR values that highly vary depending on soil properties (Zhuang et al., 2007).

C PLANTS

1 Absorption and Transport

Although Cd is considered to be a nonessential element for metabolic processes, it is effectively absorbed by both root and leaf systems and is also highly accumulated in soil organisms (Table 4.12). There are evidences that an appreciable fraction of Cd is taken up passively by roots, but Cd is also absorbed metabolically.⁷³⁷

The linear relationship between Cd in plant material and its concentration in growth media is often reported (Figures 17.15 and 17.16). Several soil and plant parameters affect the plant uptake of Cd. The variable ability of plants to take up Cd from a calcareous soil treated with 0.1 and 5 mg Cd/kg soil in sewage sludge is presented by McGrath.¹⁴⁰⁶ While field bean contents of Cd (mg/kg in

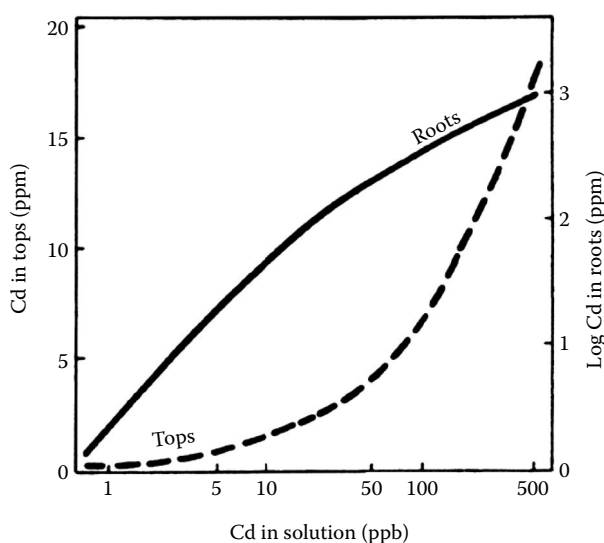


FIGURE 17.15 The effect of Cd concentration in the culture solution on Cd uptake by grass *Bromus unioloides*. (Adapted from Kabata-Pendias A., Wiacek K., *Soil Sci. Ann.*, 36/4, 33, 1985.)

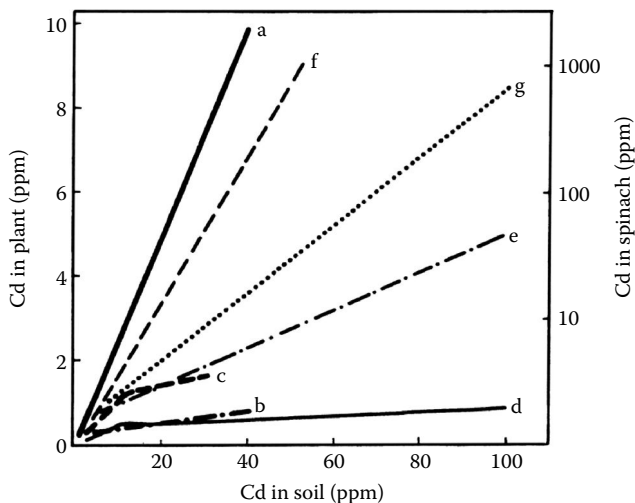


FIGURE 17.16 Cd uptake by plants from soil contaminated by this metal. (a) Potato stalks, (b) potato tubers, (c) wheat grains, (d) brown rice, submerged during growth period, (e) brown rice, drained after tillering stage, (f) barley grains, value in $\mu\text{g/kg}$, (g) spinach leaves, data for 0.1 N HCl-soluble Cd in soil. (Data compiled from Andersson A., Hahlin M., *Swed. J. Agric. Res.*, 11, 3, 1981; Diez Th., Rosopulo A., *Z Sonderdruck Landw. Forsch.*, 33, 236, 1976; Imura K., et al., *Proc. Inst. Sem. SEFMA*, Tokyo, 357, 1977; Itoh S., Yumura Y., *Bull. Veg. Ornamental Crops Res. Stn.*, 6a, 123, (Ja) 1979.)

edible tissue) were at levels <0.1 and 0.4 , carrot contained 0.9 and 8.2 , lettuce contained 1.4 and 21 , and spinach contained 3.6 and 91 , respectively. According to Jalali and Khanlari (2008), mobile Cd fraction in calcareous soils under vegetable fields was higher than the other management practices, which suggest an anthropogenic Cd source in soils under vegetables.

In many publications on this topic, soil pH is listed as the major soil factor controlling both total and relative uptake of Cd (Figure 17.17). Kitagishi and Yamane³⁹⁵ reported results of their experiment, indicating that the relative uptake of Cd by rice seedlings was the greatest at the pH range of 4.5 – 5.5 . Bingham et al.⁷⁷ also found that the Cd content of rice grain is highly dependent upon the soil pH and is the highest at pH 5.5 . However, there are contradictory results, which show that when Cd becomes more mobile in alkaline soil due to the formation of complexes or metal chelates, the plant uptake of Cd may be independent of the pH.^{41,129} Kitagishi and Yamane³⁹⁵ described that when the redox potential of soils decreases to about 20.14 V, the proportion of soluble Cd decreases,

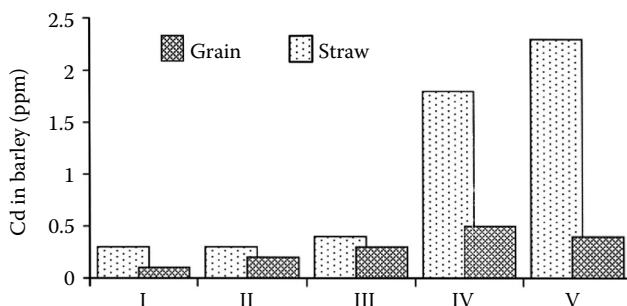


FIGURE 17.17 (a) Effect of soil pH on Cd content of soybean leaves and (b) effect of solution pH on relative Cd absorption by rice seedlings. (Data compiled from Chaney R. L., Hornick S. B., *Int. Cadmium Conf.*, San Francisco, January 31, 125, 1977; Kitagishi K., Yamane I., eds., *Heavy Metal Pollution in Soils of Japan*, Japan Science Society Press, Tokyo, 302, 1981.)

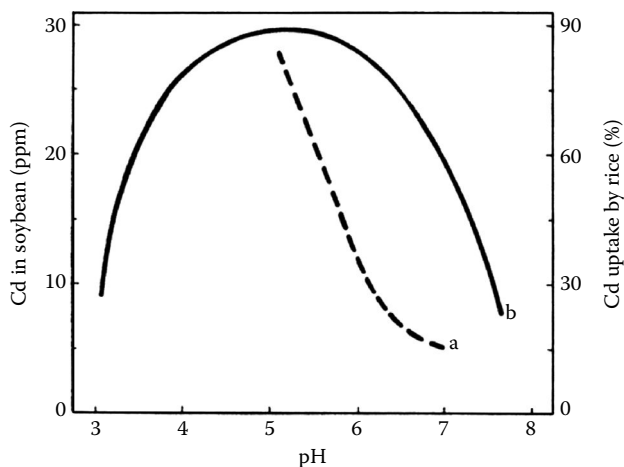


FIGURE 17.18 Impact of Cd added, as Zn and Pb smelter flue-dust, to the soil on the concentration of Cd in spring barley grain and straw. Cd levels in soils (mg/kg): I, 0.7 (blank); II, 3.7; III, 7.7; IV, 50.7; V, 100.7. (From Kabata-Pendias A., Pendias H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 1999, 400 (Po). With permission.)

corresponding to the reduction of sulfate to sulfides. This is well illustrated in a much lower uptake of Cd by rice grown in submerged soil than in soil drained after the tillering stage (Figure 17.16). Even at the high soil pH (7.2–7.8), Cd uptake by barley was a function of its content in soil. The rapid increase in the Cd concentration in straw at the 0.5 mg/kg level, and in grains at the 0.3 mg/kg level (Figure 17.18) is most probably related to a break of the physiological barrier controlling a metabolic absorption of this metal.

Although soil characteristics other than the pH can also cause differences in the Cd absorption by roots, it may be stated that soluble species of Cd in soil are always easily available to plants. Poelstra et al.¹¹²¹ described that the calculation of Cd uptake by vegetation from soils of variable conditions is difficult and uncertain. Nevertheless, Verma et al. (2007) tried to include soil and plant parameters for a model that can be used for predicting Cd accumulation in vegetables. Findings of Hornburg and Bümmer¹⁰²⁹ indicated that Cd concentrations in wheat grains increase linearly with the total Cd content of soils (Figure 17.19). Besides, a worldwide experiment carried out in 30 countries with young wheat ($N = 51,723$) and young corn plants ($N = 51,892$) indicates that plant Cd is a function of soil Cd.¹⁴⁹¹ The content of clay fraction proved to be the most important factor, among six investigated soil parameters, controlling the Cd uptake by plants. The frequency distribution of Cd contents of both plants indicated that the most common (ca 15%) concentrations range from 0.03 to 0.1 mg/kg. Results of this research program clearly indicated the effect of P fertilization on increased levels of plant Cd and soil Cd. Effects of the phosphate application rates of 3 years prior to sampling were as follows: at 10 and 50 kg P/ha rates, plants contain 0.06 and 0.1 mg/kg Cd, respectively. Effectiveness of liming to minimize the Cd uptake by cereals are also reported.¹⁴⁴⁴ However, the response was variable, and in some cases raising soil pH to 6.0 was not sufficient to decrease the Cd concentration in grain below 0.05 mg/kg (MAC value), and would not be considered economically acceptable in several areas.

Increasing Cl concentration in soil solution (due to P fertilizers, or biosolid amendment) increases CdCl^+ contents, and thus the phytoavailability of this metal (Wegglar et al., 2004). Moreover, N fertilization is reported to increase Cd concentration in soil solution and to increase its content in wheat grains (Wångstrand et al., 2007). Data from several experiments indicate that soil salinity effects may dominate soil pH effects on the Cd uptake by plants, which is especially observed in potato tubers. McLaughlin et al.¹⁴¹¹ reported that plants, especially sunflowers and potatoes, take up significantly more Cd from salt-affected soils. Chloride forms strong complexes with Cd (e.g.,

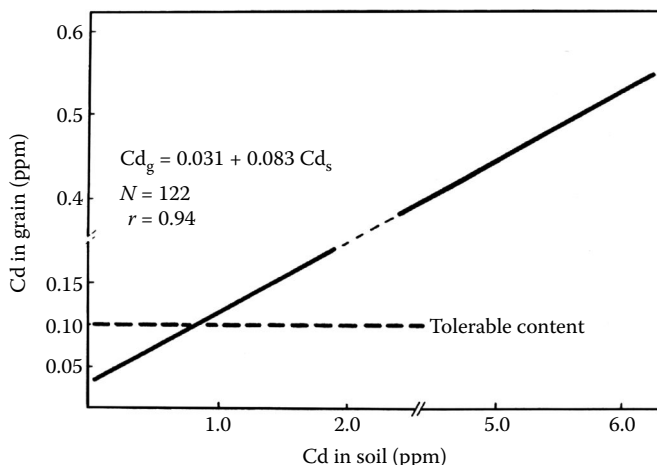


FIGURE 17.19 Relation between the Cd content of wheat grain (Cd_g) and the total content of Cd in soil (Cd_s). (Modified from Hornburg V., Brümmer G.W., *5th Spurenelement Symposium on Iodine and other Trace Elements*, F. Schiller University, Jena, 916, 1986.)

$CdCl^+$, $CdCl_2^0$, $CdCl_3^-$, and $CdCl_4^{2-}$) and therefore mobilizes and increases its phytoavailability. Sunflower is proposed for the remediation of Cd-polluted soils (Mani et al., 2007). Reported increase of Cd content in sunflower seeds was from 0.41 to 1.12 mg/kg on control and Cl-enriched soils, respectively.¹³⁸⁸

High Cd concentration in red-algal compost (3.5 mg/kg) affected increased Cd uptake by crops, with the highest transfer factor for lettuce (Greger et al., 2007). Availability of Cd from sewage sludge is highly controlled by soil pH, therefore the PMTC for Cd in sewage sludge may vary from 0.5 to 1.5 mg/kg for soil of pH 5–6, and of pH ≥ 7 , respectively (Chaudri et al., 2007).

Mench¹⁴¹³ reviewed changes in Cd availability in relation to major long-term changes in the agronomy system, and concluded that cropping systems and fertilizing affect Cd concentrations in potato tubers and cereal grains, which are the major plant-derived diet of the European population. The Cd origin is an additional important factor controlling its solubility and phytoavailability. According to Grupe and Kuntze,¹⁰¹⁹ oats absorb a much higher proportion of the anthropogenic Cd (added as Cd oxides) than that of the lithogenic origin (Figure 2.2). Filipiński⁹⁹³ calculated that spinach uptake about 3 times more Cd from the anthropogenic source than from the pedogenic one.

Variable parameters of rhizospheres might markedly alter the Cd availability due to root exudates (Dong et al., 2007a). Dell’Amino et al. (2008) inoculated plant (*Brassica napus*) with bacteria isolated from metal-polluted rhizosphere and observed a better growth of plant and resistance to Cd accumulated in plant tissues, probably due to the activity of some enzymes and production of siderophores. Cieśliński et al.¹²⁶² also reported the influence of low-molecular-weight organic acids present in the rhizosphere of durum wheat on the mobility of particulate-bound Cd and on the metal accumulation.

The Cd contents increased up to 2.3 mg/kg and 2.8 mg/kg in winter and spring wheat grain, respectively, when grown on soil with KCl addition (control value, 0.18 and 0.16 mg/kg); whereas this increase was up to 2.03 and 1.49 mg/kg on soil amended with K_2SO_4 (control value, 0.10 and 0.16 mg/kg).¹⁵¹⁰ A remarkable increase in Cd concentration in soil solution affected by NaCl is responsible for a high Cd uptake by crop plants.¹⁵⁰² Peat and phosphate amendments are known to inhibit the Cd uptake by crop plants.¹²³⁵ On the contrary, an increased Cd availability to crops on a sewage-sludge-amended soil does not indicate an immobilization of Cd under the influence of increased SOM content.¹⁵¹⁷ However, results of the experiment carried out by Singh and Myhr¹⁴⁹⁷ did not show any significant effect on its concentration in barley grain when Cd was applied to a soil in various forms.

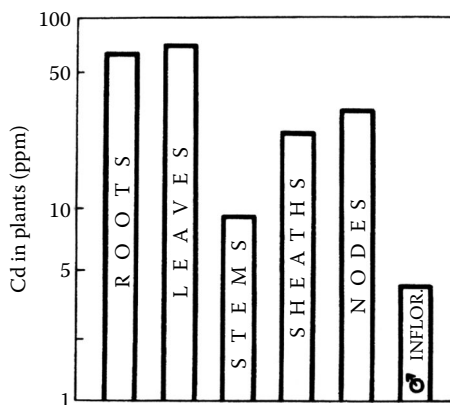


FIGURE 17.20 Distribution of Cd in corn plants grown in the soil with 15 mg/kg Cd. (Adapted from Kabata-Pendias A., Wiacek K., *Soil Sci. Ann.*, 36/4, 33, 1985.)

Chaney and Hornick¹²⁹ reviewed plant response to increased levels of Cd in soil and showed a great difference in the ability of various plant species to absorb this metal. The difference in Cd content of crops grown in the same soil with Cd level at 10 mg/kg exceeded 100-fold; the lowest concentration was in rice plants, Sudan grass, and clover, and the highest was in spinach and turnip. On the contrary, Simmons et al. (2003) reported much higher Cd accumulation in rice grains than in soybean grains. The distribution of Cd within plant organs is quite variable and clearly illustrates its rapid transport from roots to tops and, in particular, to leaves (Figure 17.20). The Cd distribution in strawberries, however, indicates rather a low rate of its transport from roots to above-earth parts of plants. The following Cd concentrations were found in strawberries grown in soil with 60 mg/kg Cd and neutral pH (in mg/kg): roots, 191–509; leaves, 3.7–8.9; and fruits, 0.15–0.7 g.¹²⁶¹ Cunningham et al.¹⁵⁵ reported that increased Cd²⁺ treatment progressively suppressed the proportion of Cd translocation to epigeal parts of young leaves and that Cd was localized mainly in roots, with lesser amounts in stem nodes, petioles, and major leaf veins. According to Majewska and Kurek (2008), grass (*Festuca ovina*) roots accumulate more Cd than cereal (*Secale cereale*) roots and transport much more Cd to the above-ground parts than do cereals.

Tiffin⁷⁸⁹ found the ¹⁰⁹Cd concentration in tomato xylem exudates to be from 1.5 to 3.5 μM/L, after treatment with this radionuclide. This suggests that Cd, as other trace metals, can be easily transported within a plant in the form of metallo-organic complexes. A great proportion of the Cd is known to be accumulated in root tissues, even when Cd enters the plant via foliar systems.³⁷⁶ This, however, was not reported for rice plants when ¹⁰⁹Cd was applied to leaves.³⁹⁵

2 Biochemical Functions

The most important biochemical characteristic of Cd ions is their strong affinity to sulfhydryl groups of several compounds (e.g., Cd complexes with metallothionein-like proteins). Dabin et al.¹⁶¹ and Braude et al.¹⁰² reported that Cd is likely to be concentrated in the protein fractions of plants. In tomato roots, Cd is accumulated in the form of Cd–phytochelatin complex (Ben Amur et al., 2008). Cd also shows an affinity for other chains of proteins and for phosphate groups. Pavliková et al. (2002a) reported that majority of Cd in spinach is associated with various polypeptides and phytochelatin (oligomers of glutathione), as well as with cell walls and cytoskeleton. Plaza and Bovet (2008) described a function of ABC proteins as transporters of Cd into the vacuoles and thus detoxifying the Cd excess.

There are unknown enzymes that depend on the Cd for their normal activity. Roucoux and Dabin⁶⁶⁶ reported that Cd specifically induced cysteine and methionine synthesis in soybeans,

depending on the degree of plant resistance to increased Cd levels. It is considered to be a toxic element to plants, and the basic cause of its toxicity lies in its disturbing enzyme activities. A decline in glutathione contents is observed in tissues of tomato exposed to Cd (Ben Amur et al., 2008). Rellán-Alvarez et al. (2006) also reported oxidative stress in corn plants due to reduced glutathione level. Increase in the ascorbate–glutathione metabolism improved plant tolerance to the Cd stress (Paradiso et al., 2008). An addition of S to soil resulted in Cd decrease in mustard plants and increased content of ascorbate and glutathione (Anjum et al., 2008). Cunningham et al.¹⁵⁵ and Baszynski et al.⁵⁴ reported inhibition of the formation of anthocyanin and chlorophyll pigments in plants that were treated with Cd. Excess of Cd may affect cell acidosis, due to an imbalance in H^+ production associated with changes in anaplerotic reactions (Nocito et al., 2008). Root-selective expression of AtCAX4 and AtCAX2 (calcium exchangers) play a role in plant (*Nicotiana tabacum* L.) tolerance possibly due to the vacuolar Cd sequestration (Korenkov et al., 2007). As Fusconi et al. (2007) described, Cd stress affects cell biology (viability, proliferation) and cell structure (microtubules). According to Wierzbicka et al. (2007), Cd is detoxified in plant cells mainly by organic acids.

The amount of chlorophyll was found to be a function of the Cd concentration in plant tissues and has been proposed as an indicator of the upper critical Cd level in plants.⁹⁵⁸ Kloke et al.¹⁰⁵² estimated the phytotoxic concentrations of Cd to be 5–10 mg/kg in sensitive plant species, whereas Macnicol and Beckett¹⁰⁸¹ gave the range of 10–20 mg/kg as critical Cd levels. The response of bean plants to Cd in growth media depends on the age of plants and time of Cd action. With plant aging, their sensitivity to Cd increases and is more related to functioning of the photosynthetic apparatus than to growth parameters. As Skórzynska-Pilot and Baszyński¹⁴⁹⁹ reported, changes in growth parameters are observed in young plants but photosynthetic activity is almost unchanged. Elevated concentrations of Cd in the rooting medium of barley affected the increase of shoot thionein mRNA, which is similar to the effect of a pathogen attack.¹³⁷⁸

In general, overt symptoms induced by elevated Cd contents of plants are growth retardation and root damage, chlorosis of leaves, and red–brown coloration of leaf margins or veins (Table 5.8). The phytotoxicity of Cd, beyond interfering with normal metabolism of some micronutrients, shows inhibitory effects on photosynthesis, disturbs transpiration and CO_2 fixation, and alters the permeability of cell membranes (Prasad, 2005). Due to increasing elastic modules and cell wall electricity, Cd reduces water transport in plants and such decreases water stress tolerance of plants (Prasad, 2008). The Cd toxicity also results in disturbed stomatal conductance and the electron transport system.

The Cd excess has a complex inhibitory impact on the Calvin's cycle, and especially disturbs a function of the key enzyme, ribulose, diphosphate, and carboxyhydrazine. Photochemical activities of chloroplasts are significantly reduced at the Cd concentrations of 50–75 $\mu M/L$ in nutrient media.¹⁵²³ Cd is also known to inhibit the DNA-mediated transformation in microorganisms and to interfere with symbiosis between microbes and plants, as well as to increase plant predisposition to fungal invasion. McKenney and Vrisacker¹⁰⁹⁰ found that Cd is an effective and specific inhibitor of the biological reduction of NO_3^- to NO . However, even at a high Cd content of soils, a slow adaptation of some streptomycetes species was observed.¹⁰⁴⁹

3 Interactions with Other Elements

Plants are simultaneously exposed to a variety of pollutants, and thus their integrated effects most often are different from the effect of Cd only. Several elements are known to interact with Cd in both element uptake by plants and their biochemical roles.

Cd–Zn interactions are commonly observed, but findings appear contradictory, since both depressing and enhancing effects of each metal have been reported. The interaction of Cd and Zn has received much study, and all findings may be summed up by stating that, in most cases, Zn reduces the uptake of Cd by both root and foliar systems. Chaney and Hornick¹²⁹ suggested that when the Cd:Zn ratio in plant tissues is limited to 1%, the Cd content is restricted to below 5 mg/kg,

thus below its phytotoxic level. Babich and Stotzky⁴¹ described the double antagonistic interactions between Cd–Zn and Cd–Mg in microorganisms. However, results of some studies indicate that increased Zn supply to growth media does not inhibit the Cd accumulation by plants (Grant and Bailey, 1997). Nan et al. (2002) concluded that Cd–Zn interaction is synergistic under field condition, thus increasing both metals in soils affect their increased accumulation in plants.

Cd–Cu interactions are also complex. The inhibitory effect of Cu on Cd absorption is reported most often.

Cd–Mn/Ni interactions also are often reported and appear to be related to their replacement by Cd during the uptake processes.

Cd–Fe interactions are related to disturbances in the photosynthetic apparatus. Only a moderate excess of Fe has a detoxificatory influence on Cd-treated plants, although a higher dose is toxic. Effects of Cd–Fe interaction on the photosynthesis is most probably of an indirect nature.¹⁴⁸⁹

Cd–Se mutual antagonistic effects were observed in certain crops. According to Feroci et al. (2005), seleno-urea forms a complex with Cd²⁺ of limited solubility, which might decrease its availability.

Cd–P interactions are exhibited in the P effects on Cd uptake by plants. Both increased and decreased contents of Cd under phosphate treatment are reported. Apparently, these reactions take place in the root media, and thus, the influence of the P supply on soils might differ for various soils and crops. It is most likely that Cd–P interactions may be similar to those in the Zn–P relationship.

Cd–Ca relationship seems to be highly cross-linked with variation in the soil pH. It cannot be precluded, however, that Ca²⁺ ions are able to replace Cd²⁺ in carrier mechanisms and thus Cd absorption by plants may be inhibited by an excess of Ca cations.

Cadmium uptake–translocation mechanisms are reported to be influenced by the supply of other nutrients such as K, N, and Al, but results are variable and may be related to some secondary effects.

Interactions of Cd with several essential elements (e.g., Mg and K) are observed and may be related to an impaired effect of Cd on the cell membrane, which disturbs their uptake and transport within plant organs. An antagonistic impact of Cd on the P absorption by plants is significant for plant growth and agricultural practices. The P uptake by plants can be reduced up to 40% of control values.

4 Concentrations in Plants

The Cd content of plants is of great concern as a pathway of Cd to man and animals. Thus, tolerance and adaptation of some plant species to higher Cd levels, although important from an environmental point of view, create a health risk. Therefore, Cd contents in plants, food, and fodder plants, in particular, have been widely studied.

A comparison of the Cd contents of plant foodstuffs produced under uncontaminated conditions of various countries shows the highest Cd concentration not only in leafy vegetables, but also in carrot and potatoes (Table 17.8). When various plants are grown in contaminated soil, Cd is very likely to also be concentrated, especially in roots (Table 17.9). Cd concentration in food plants is of special concern and several international organizations have been collaborating to protect human health and the environment from the Cd stress. According to the EC Commission Regulation (2006), the maximum levels for Cd are (in mg/kg FW) for: (1) most cereal grains, 0.10; (2) most vegetables, including potatoes, 0.05; and (3) leafy vegetables and mushrooms, 0.20. The highest contribution of Cd in the diet in Germany is calculated (in % of Recommended Dietary Allowance (RDA)) for cereal bread as 13.3% and for potatoes as 5.7%.¹²⁴⁷ In Japan, rice is the major source of Cd in the diet.

The Cd background levels of common food and fodder plants that are reported for various countries are fairly low, and surprisingly similar, within the general range in cereals grains of 0.005–0.252 mg/kg (Tables 17.8 and 17.9). Data for cereal grains in Poland gave the mean Cd content as 0.06 mg/kg.^{1416,1514} The median Cd concentration in wheat grains from France is 0.045 mg/kg (range,

TABLE 17.8
Cadmium in Food Plants Grown in Various Countries^a
(mg/kg)

Plant	Range or Mean
Cereal, grains ^b	0.005–0.032
Wheat, grains	0.02–0.07
Wheat, grains ^c	0.002–0.252
Barley, grains	0.013–0.022
Legumes	0.001–0.03
Broccoli	0.01
Cabbage	0.005–0.01
Lettuce	0.029–0.4
Carrot	0.03–0.24
Onion	0.08
Potato	0.016–0.3
Tomato	0.03
Spinach	0.043–0.15

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b After Eriksson (2001), data for Sweden, mean values for barley and wheat, respectively.

^c After Škrbić and Onjia (2007), data for Serbia.

0.015–0.165 mg/kg).¹²¹³ The average Cd concentration in wheat grain collected in Germany is 0.057 mg/kg (FW).¹²⁴⁷ Wheat grain of the United States has an average Cd concentration of 0.03 mg/kg (FW).¹⁵⁴⁹ Hornburg and Brümmer¹⁰²⁹ reported that the Cd content of wheat grain is highly correlated with the Cd concentrations in the plow layer (Figure 17.19). Adams et al. (2004) proposed the model, based on soil Cd and pH, for predicting Cd concentrations in wheat and barley grain.

Potato stalks and tubers are especially susceptible to increased levels of Cd, and potatoes are considered a major source of Cd in diets of several human populations.¹⁴⁵⁵ Therefore, the Cd concentration in potatoes is monitored in some countries. Potato tubers (washed, unpeeled) sampled from the whole territory of Poland contained an average of 0.11 mg/kg of Cd,^{1416,1357} and potato tubers collected in Germany had 0.108 mg/kg.¹²⁴⁷ A median value for Cd in potato tubers on a state basis for the United States is 0.028 mg/kg (FW), which roughly corresponds to 0.15 mg/kg (DW).¹⁴¹¹

At present, special attention is given to Cd contents of carrot roots, which have a major use in baby foods. Especially that carrot fields are highly fertilized with phosphates. The average Cd concentrations in commercially grown carrots in different countries is (in mg/kg FW) as follows: Sweden 0.32; Romania (industrial region) 0.23; Poland (industrial region) 0.20, and (rural region) 0.04.¹³⁵⁷

Because Cd is readily available to plants from both air and soil sources, its concentration rapidly increases in plants grown in polluted areas. Data collected for several countries show that both industrial and agronomic practices might create a significant Cd supply to plants (Table 17.9). The highest concentrations of Cd in polluted plants were always reported for roots and leaves, whereas Cd seems to be excluded from seed crops. The highest Cd values reported for wheat grains (14.2 mg/kg) and brown rice (5.2 mg/kg) were less than the amounts of the metal accumulated in root and leaf tissues of these plants.

The distribution of Cd in forest ecosystems is of special environmental concern. Cd is likely to be concentrated in the outer parts of conifer trees (spruce and pine), phloem, and bark (up to 1.3 mg/kg),

TABLE 17.9
Excessive Levels of Cadmium in Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Part	Mean or Range	Country	Reference
Ancient mining area	Grass	1.0–1.6	Belgium	728
	Lichens	11–22	Belgium	728
	Brussels sprouts	0.10–1.77	Great Britain	168
	Grass	1.1–2.0	Great Britain	513
	Clover	4.9	Great Britain	513
Metal-processing industry	Lettuce	45	Australia	57
	Silver beet, leaves	0.04–0.49 ^a	Australia	793a
	Turnip, leaves	0.5	Germany	430
	Grass	8.2	Great Britain	1005
	Brown rice, grain	0.72–4.17	Japan	395, 891
	Lettuce	5.2–14.1	Poland	224
	Carrot roots	1.7–3.7	Poland	224
	Spinach	6.4	Zambia	573
	Wheat grain	0.22–0.47	Poland	1510
	Mushrooms ^d	3–56	Finland	1069
Lignite coal-fired power station	Grass	1.1	Czech Republic	655
Urban garden	Brussels sprouts	1.2–1.7	Great Britain	786
	Cabbage outer leaves	1.1–3.8	Great Britain	786
	Lettuce	0.9–7.0	U.S.	627
Sludged, irrigated, or fertilized farmland	Cereal, grains	0.1–1.1	Finland	748
	Brown rice, grains	5.2 (max.)	Japan	336
	Sudan grass	0.3–2.9	Hungary	1177
	Lettuce ^b	70	U.S.	789
	Lettuce	8–37	Germany	947
	Corn ^b	35	U.S.	789
	Lettuce	0.5–22.8	U.S.	127
	Carrot roots	0.2–3.3	U.S.	127
	Soybean seeds	2.3	U.S.	102
	Cabbage leaves	130	Russia	826
	Wheat grains	5.5–14.2 ^c	Russia	338
	Wheat leaves	19–47 ^c	Russia	338
	Wheat roots	397–898 ^c	Russia	338
Airborne contamination	Lettuce	5.2	Denmark	625
	Spinach	3.9	Denmark	625
	Carrot roots	3.5	Denmark	625

^a FW basis.

^b Diagnostic leaf.

^c Pot experiment.

^d *Boletus edulis*.

which leads to its accumulation in wood ash up to 30 mg/kg. In the wood ash of willow, Cd contents can reach 70 mg/kg.¹³⁹¹ Mushrooms reveal a great affinity to absorb Cd from growth media. Lepp et al.¹⁰⁶⁰ gave as an example a mushroom (*Amanita muscaria*) containing Cd at 29.9 mg/kg, and growing in soils of an unpolluted woodland with a relatively low Cd content (0.34 mg/kg). Nuorteva^{1104a} reported high Cd contents (12–24 mg/kg) of fruit bodies of some mushrooms also growing in unpolluted forest in Finland.

TABLE 17.10
Mean Levels and Ranges of Cadmium in Grasses and Legumes at the
Immature Growth Stage from Different Countries (mg/kg)

Country	Grasses		Clovers		Reference
	Range	Mean	Range	Mean	
Canada	—	0.21	—	0.28 ^a	497
Czech Republic	—	0.6	—	—	655
France	—	0.16	—	0.11 ^a	577
Germany	0.05–1.26	0.27	0.02–0.35	0.16	430, 488
Germany	0.03–0.14	0.07	0.04–0.18	0.08 ^a	577
Iceland	0.07–0.14	0.10	—	—	577
Poland	0.05–1.25	0.32 ^b	0.07–1.0	0.46 ^c	1045
U.S.	0.03–0.3	0.16	0.02–0.2 ^a	—	330a, 704
Kazakhstan	0.1–0.55	0.22	—	—	1131

^a Alfalfa.

^b Orchard grass.

^c White clover.

Cadmium levels in legume plants (clovers) and grasses are fairly similar in various countries (Table 17.10). The ranges of mean values are (in mg/kg) 0.07–0.27 and 0.8–0.46, for grasses and clover, respectively.

III MERCURY

A INTRODUCTION

Mercury has been known since prehistorical times and used by alchemists in China since 2000 BC. For over a century it has been known as an environmental pollutant. Release of Me–Hg in the industrial wastewater resulted in Minamata disease (neurological damage) in Japan in 1959. A loss of IQ points is presently observed under the Hg exposure.

The crustal Hg average content is 0.07 mg/kg (Table 3.2). Its abundance in igneous rocks (0.004–0.08 mg/kg) is lower than in sedimentary rocks (0.01–0.4 mg/kg) and is mainly concentrated in argillaceous sediments (Table 17.2). The Hg geochemistry is intimately connected with its chalcophil character. Its main commercial ore is cinnabar (metacinnabar), HgS. Besides, sulfide, selenide, telluride, and so on, of Hg are in various ore deposits. Metallic alloys of Hg with other metals (e.g., Ag and Pd), oxides (e.g., montroidite and HgO), and organic Hg complexes are also found as minerals. There are several Hg host minerals such as amphiboles, sphene, sphalerite, and other sulfides.

The most important geochemical features of Hg are as follows:

- Affinity to form strong bonds with S (e.g., cinnabar and HgS)
- Formation of organomercury compounds, which are relatively stable in aqueous media
- Formation gaseous compounds (Me–Hg)
- Volatility of elemental Hg

As the chalcophile metal, Hg shows affinity to other metals, such as Ag, Zn, and Cd. The mercuric salts (e.g., HgCl₂) are soluble in water whereas organomercurics are neither soluble nor do they react with weak acids and bases due to a low affinity of Hg for oxygen bound. In the environment, Hg occurs in various chemical and physical forms, such as Hg⁰, HgCl₂, HgO, HgS, CH₃HgCl, and (CH₃)₂Hg, and each species behaves differently in various ecosystems (Drasch et al., 2004).

The global annual Hg production in 2000 was estimated as 1.8 kt (Drasch et al., 2004), and in 2008 as 0.95 kt (USDI, 2009). Jernelöv and Ramel (1998) emphasized, however, a disagreement between the established global Hg production and the use of Hg that was about twice higher during 1991–1995. Due to the toxic properties of Hg and the strict regulations, primary Hg production and its uses were restricted in many countries. In some countries, the Hg production was lowered or completely stopped (Ferrara, 1999).

Major uses of Hg are in (1) chlor-alkali production, (2) vinyl chloride monomer production, (3) artisanal gold mining, and (4) batteries, control instruments, and electrical lightings production. Increased Hg load into the environment, due to its use in Au mines for amalgamation process, became of a real environmental concern. This is a serious threat in the Amazonian region and in the Siberian subregion (Jernelöv and Ramel, 1998). Traditional uses of Hg for dental fillings, measuring instruments, batteries, florescent lamps, wood impregnation, paints, and pesticides have been forbidden in recent years in some countries.

Mercury is considered a global pollutant. The US Clean Air Act Amendments, in 1990, have identified Hg as one of the trace elements listed in the legislation as “hazardous air pollutant” because of its toxicity, availability, potential bio-accumulation within the environmental compartments, and human health risk (Petersen et al., 1998). The discussion on environmental and socio-economic costs of Hg pollution has been undertaken and needs for limiting its emission is discussed (Hylander and Goodsite, 2006). Hylander and Meili (2005) emphasized that current challenge is the disposal of the large Hg stocks used as electrodes in chlor-alkali plants, especially in the EU countries. Current issue on Hg in the environment, its fate and transport in the global atmosphere, is presented by Pacyna et al. (2008) Mercury emission from industrial sources, and from coal combustion, in particular, is of a great environmental concern (Pirrone and Mason, 2009). Hg content of some coal might be up to 10 mg/kg (Finkelman, 1999). Current anthropogenic Hg sources is calculated on an annual basis at about 2909 t, and its emission from fossil-fuel-fired power plants is given as 1422 t (Pirrone et al., 2009).

B SOILS

The average content of Hg in soils of different groups all over the world range between 0.58 and 1.8 mg/kg, and the worldwide mean content is estimated as 1.1 mg/kg (Table 3.2). Its higher concentrations are in Histosols and Cambisols (Table 17.2).

The Hg content of virgin soil is inherited mostly from the parent material. However, because Hg is easily volatile, some additional natural sources, such as degassing and thermal activity of the Earth, cannot be precluded. The Hg accumulation is related to organic C and S levels in soils and is concentrated in surface soils at several times the concentration in subsoils. Generally, Histosols have a higher Hg content than mineral soils. This is mainly due to a great capacity of SOM, especially of raw humus, for binding Hg. Johansson et al.¹⁰⁴¹ reported high Hg concentrations in raw humus, often exceeding 0.3 mg/kg. These authors assumed that the original level (baseline) was about 0.1 mg/kg, and they related this increase of Hg mainly to its atmospheric deposition. The sorption of Hg varies with pH, the highest being at pH from 4 to 5.^{1143,1163} Soils have a greater capacity for organic Hg than for HgCl_2 ; however, the sorption of all Hg compounds is positively correlated with the organic C and CEC of soils. Its concentration in the soil solution is very low, at about 2.5 $\mu\text{g/L}$, and preferable as cationic species such as Hg_2^{2+} , HgCl^+ , and HgCH_3^- . However, it also can form anions, such as HgCl_3^- and HgS_2^{2-} (Kabata-Pendias and Sadurski, 2004).

The background levels of Hg in soils are not easy to estimate due to the widespread Hg pollution. Nevertheless, data reported for various soils on a worldwide basis show that mean concentrations of Hg in surface soils do not exceed 1.5 mg/kg (Table 17.2). Most top soils, however, contain increased amounts of Hg, especially near mining and smelting areas (Table 17.11). The highest mean levels of Hg are reported (in mg/kg) for Histosols of Canada, 0.4; and paddy soils of Japan, 0.35, and Vietnam, 0.3. Similarly, in organic and clay soils of the United States, the highest average concentrations were

TABLE 17.11
Mercury Contamination of Surface Soils (mg/kg)

Site and Pollution Source	Maximum or Range of Content	Country	Reference
Ancient mining area	0.21–3.4	Great Britain	164a, 165
Hg mining or ore deposit	0.2–1.9	Canada	368
	0.09–0.22	Brazil	1467
	54	Czech Republic	1114
	0.6–4.2	Yugoslavia	413, 414
	2.6–2.9	France ^c	1463
	8.2–40	U.S.	79, 703
	0.1–5.6	Russia	198, 1396
Chlor-alkali or chemical works	3.8	Great Britain	111
	17, 100	Kazakhstan	Randall et al. (2004)
	0.32–5.7	Canada	776
	0.06–0.495	Egypt	990
	0.10–0.43	Switzerland	637
	0.08–0.26	France	1463
Urban garden and park	0.03–1.14	Canada	243
	0.25–15.0	Great Britain	488a, 850
	0.6	Great Britain	634
	0.6	U.S.	208
	0.04–0.08	Israel	724
	0.06–0.24	Japan	277
Sludged or irrigated farmland	10.0 ^a	Holland	223
	0.03–0.15	Hungary	1177
	0.43–24	Germany	205, 947, 1023
	0.29–0.71	Japan	395
	0.8	Sweden	25
	0.68–1.43 ^b	U.S.	1186
	0.12–0.35	Poland	162
Application of fungicides	9.4–11.5	Canada	498
Volcanic area	0.041–7.45	Italy (Etna)	931
	0.001–0.023	U.S. (Mt. St. Helens)	1146

^a Soil flooded by Rhine River water.

^b Nine years after sewage sludge application at rate 33 and 180 t/ha, respectively.

^c Alluvial soils downstream from the ancient industrial Hg pollution.

found to be 0.28 and 0.13 mg/kg in Histosols and Cambisols, respectively. Apparently, organic soils and paddy soils are likely to retain Hg more than any other soils, that resulting from vegetable decay and absorption from the atmosphere. The range of Hg in reference soils of China is from 0.015 to 0.294 mg/kg (mean, 0.142).¹³¹³ The mean content of total Hg in agricultural surface soils and forest soils of Poland is estimated at 0.06 mg/kg (range 0.03–0.284), with the highest concentration in forest soils near the Nitrogen Fertilizers Works.¹²⁷⁴ The range of Hg in urban soils of Poland is 0.13–0.5 mg/kg.¹²⁹⁷ Soils in the vicinity of a cement plant do not have increased Hg levels, which is within the range of 0.01–0.03 mg/kg (Jaworska et al., 2009). Guedron et al. (2006) estimated that in tropical soils of French Guiana, the content of lithogenic (from parent material) Hg is below 0.04 mg/kg, whereas exogenic Hg (from atmospheric input) is up to 0.5 mg/kg. Baseline levels for Hg in soils from Belgium vary between 0.09–0.43 and 0.7–0.15 mg/kg, from region with industries employing

Hg and other areas, respectively (Tack et al., 2005). The very broad Hg range, 0.004–1.510 mg/kg, is reported for suburban soils of China (Zhao et al., 2008). Relatively high Hg contents, up to 98 mg/kg (at an average 0.08 mg/kg), are reported for some top soils of the Slovak Republic (Čurlik and Šefčík, 1999).

According to a general calculation, about 1–3% of total Hg in surface soils is in the Me–Hg forms and the rest may be considered as Hg^{2+} complexes. Some properties of Hg species in soils are as follows:

- Easy volatilization: Hg^0 and $(\text{CH}_3)_2\text{Hg}$
- Easy solubilization: HgCl_2 , $\text{Hg}(\text{OH})\text{Cl}$, and $\text{Hg}(\text{OH})_2$
- Low mobility: CH_3Hg^+ and CH_3HgS^-
- Nonreactive species: HgS , $\text{Hg}(\text{CN})_2$, and Hg^{2+} bound to some OM

The Hg behavior in soils depends highly on its form, which is a function of several soil parameters, and of initial Hg concentration in soil solution, as well as of other ions (e.g., Cl).¹⁵⁶² Simple cations of Hg dominate in aerobic soil conditions. Complex anions of Hg with S are likely to occur in anoxic soil conditions, whereas methylated Hg compounds predominate in soils of intermediate redox states.

Although Hg may form several ionic species (Figure 17.21), it is not very mobile during weathering (Table 3.4). As Jonasson,³⁶⁷ Shcherbakov et al.,^{715a} and Landa⁴⁵⁸ reported, Hg is likely to be strongly bound when added to soils as elemental Hg or as cationic or anionic complexes. Mercury ions (Hg_2^{2+}) generally form weaker complexes than do mercury ions (Hg^{2+}). Hg is retained by soils mainly as slightly mobile organocomplexes. The increased Hg in decomposing deciduous litter suggests its translocation from soil to decomposing OM and thereby prolongs the residence time of Hg in the forest floor (Demers et al., 2007).

A broad review of Hg in soils, its distribution, speciation, and biological effects was presented by Rundgren et al.¹⁴⁷³ and Ebinghaus et al.¹²⁸⁴ The findings of Hem³¹² and of Farrah and Pickering²²⁹ clearly indicate that $\text{Hg}(\text{OH})_2$ is likely to predominate over other aqueous species at a soil pH near or above neutrality. Some investigators believe, however, that $\text{Hg}(\text{OH})_2$ is a preferred sorbed species.⁹⁴⁸ The presence of an excess of Cl^- ions in soils appears to decrease the sorption of Hg^+ onto both mineral particles (including Mn oxides) and OM, because the highly stable Hg–Cl complexes

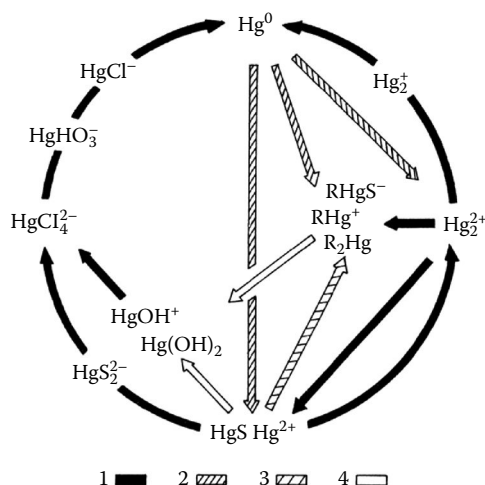


FIGURE 17.21 Ionic species and transformations of mercury compounds in soils. (1) Reduction; (2) oxidation; (3) formation of organic compounds; (4) hydration; R: CH_3 , CH_3CH_2 , C_6H_5 .

are rather poorly sorbed.⁹⁴⁸ The sorption of Hg by clays in soil seems to be relatively limited. The Hg accumulation in soil is controlled mainly by a formation of organic complex and precipitation. Thus, the Hg mobility requires dissolution processes and biological and chemical degradation of organomercury compounds.

Investigations carried out by Yin et al.¹⁵⁶² show that less than 4% of the total Hg content could be adsorbed *via* electrostatic interaction, and it is not a major driving force for Hg adsorption by soil particles. The data of these authors clearly indicate the importance of SOM in the adsorption and desorption of Hg²⁺. However, the adsorption and desorption isotherms do not follow the same track. Anoshin et al.¹²⁰³ studied Hg behavior in the environment of western Siberia, and also emphasized the significant role of OM in its distribution within soil profiles and indicated different Hg cyclings in forest ecosystems and steppe ecosystems. The studies of Malinina et al.¹³⁹⁸ indicated that suspension forms of Hg are mainly responsible for its migration in various soils of semi-humid and humid zones in Russia. Stankheev et al.¹⁵⁰³ studied Hg flow in the soil gas in earthquake areas and stated that the increase of Hg-vapor flow corresponds to the intensity of earthquakes.

The transformation of organomercury compounds, especially methylation of elemental Hg, plays the most important role in Hg cycle in the environment. The methylated Hg (Me-Hg) is readily mobile and easily taken up by living organisms, including some higher plants.^{58,359,470,856} SOM is known to mediate the chemical methylation of inorganic Hg by releasing labile methyl groups. On the contrary, a rapid conversion of organic Hg and Hg²⁺ ions to the elemental state (Hg⁰) in contact with humic substances is also reported.¹⁰⁶⁴ The mechanism of Hg methylation is still not fully understood. It can occur abiotically, and also a vast number of organisms (especially microorganisms) may carry out these reactions.

Several types of bacteria and yeasts have been shown to affect the reduction of cationic Hg²⁺ to the elemental state (Hg⁰); thus, the result of these processes is the volatilization of Hg from media. The oxidation of elemental Hg to its cationic forms can also be mediated by microorganisms. The Hg vaporization from soils is generally accelerated by microbial and nonmicrobial processes, and the volatilization rate is probably the highest when microbial processes are most intense (Andersson, 1979). Adaptation of bacteria to increased level of Hg in the floodplain soil is due to gene transfer mechanism (Oregaard and Sorensen, 2007). Clay–mineral complexes on the surface of bacterial cell walls are also considered as a mechanism of Hg resistance (Tazaki and Asada, 2007).

1 Reactions with Soil Components

In soils, the migration processes involving Hg are rather limited; therefore, the Hg content of surface soils is slowly built up, even under a low input of this metal.²⁰⁵ However, Landa⁴⁵⁹ reported Hg losses by volatilization from soils, which increased with higher soil temperature and with higher soil alkalinity. As reported by Lodenius,¹⁰⁷¹ a strong affinity of Hg to OM seems to increase with increasing soil acidity. Even in sandy soil, Hg is strongly adsorbed, and the addition of acid rain or salt solution does not increase its solubility. The Hg leaching from soils may be stimulated by factors increasing the leaching of SOM. Recent studies conducted on a large scale in Sweden showed a relative mobility of Hg in soils, especially of the Hg fraction which is bound to OM.¹⁰⁶⁴ Thus, Hg is leached out from the soil profiles in an acid environment in a form bound to organic compounds, and in neutral and slightly alkaline soils, it is leached out in an inorganic active fraction. In contrast to other trace metals, the amount of mobilized Hg decreases at pH < 3 and at pH > 12, due to the extremely high buffering capacity of SOM, in both acidic and alkaline states. Mou et al.¹⁴²⁹ estimated that the maximum Hg capacity of soil minerals and SOM is in the range of 106–474 mg/kg and 322–889 mg/kg, respectively. The humus-Hg is more easily released through evaporation and leaching than the mineral-Hg.

Kot et al.¹³⁷¹ measured Hg forms in soils and bottom sediments and concluded that the most mobile fraction of Hg bound to FA is present mainly in urban soils (up to 7% of total contents) and in bottom sediments (up to 14% of total contents). Predominating fractions of Hg, however, are those trapped by HA (26–59% of total contents) and fixed as not-hydrolyzing residue (17–66% of total contents). Kot et al. (2007) observed that addition of colloidal S immobilizes Hg in soil solution.

The authors suggested that this process occurs through Hg binding by S-bearing functional group in HA (but not FA).

According to Johansson et al.,¹⁰⁴¹ the largest amounts of Hg are transported in the autumn and spring when the water discharge is high and the Hg content and acidity of the water are elevated. They calculated the flow rate between 1 and 6 g Hg/km/year. The Hg leached from soils, together with the Hg transported from the soil with runoff and direct aerial Hg deposition onto the lake surface, has created complex and serious environmental problems.^{1041,1064} Lodén¹⁰⁷⁰ reported, however, that increased acidity of the effluent enhances the sorption of Hg to SOM, and thus decreases its leaching. Therefore, Hg is likely to be relatively strongly bound to organic compounds in acid soil conditions, and thus the Hg in acidified lakes of Scandinavian countries does not seem to be caused by an increased leaching of Hg from soils.

The affinity of Fe hydroxides to bind Hg results in a concentration of this metal in ferrallitic soils, rich in ferruginous nodules. In these types of soils, Hg distribution is associated with Fe compounds rather than with OM. Increased levels of Hg are observed in Amazonian soils with horizons enriched in Fe oxides.¹³⁰⁰ Under the processes of reduction of Fe oxides and podzolization, Hg trapped by Fe compounds is released into aquatic systems.

Various organic compounds of Hg (e.g., methyl, ethyl, and phenyl) added to soil are partly decomposed or adsorbed by soil constituents. However, all these compounds, having a relatively small degree of dissociation and adsorbability, are readily taken up by plants. According to Kitagishi and Yamane,³⁹⁵ Me–Hg was the most available, whereas phenyl- and sulfide-Hg were the least available to plants and that residue of organomercuries varied, being the highest for phenyl-Hg and Me–Hg. Compared with methylation, demethylation is a much slower process, although both biological and chemical demethylations of Me–Hg are reported.⁹⁴⁸ Inverfeldt et al.¹³⁴² observed that the rate of the Me–Hg production decreases with time, indicating that the added inorganic Hg is immobilized and unavailable for methylation, a few months after addition. The net production of Me–Hg is much faster in wetlands than in dry soil (up to 20 times). Thus, it is difficult to calculate the net production of Me–Hg considering the total Hg pool of soils. Wallschläger and Bloom¹⁵³⁵ estimated that dimethyl-Hg contributes between 1% and 15% of the total Hg emissions from wetlands. Thus, dimethyl-Hg can be considered a “carrier species” in the transport of Hg from the soils to the atmosphere, but, due to rapid decomposition, cannot serve as a simple indicator of the total Hg emission from soils. Several studies demonstrated that the addition of water significantly increases Hg release from soils, and the magnitude of its release correlates with the Hg concentration in soils (Frescholtz and Gustin, 2004). The release mechanism of Hg from soils is assumed to be due to the displacement of Hg by the more polar water molecules (Engle et al., 2001).

2 Contamination of Soil

There are several exogenic sources of Hg, and most of them are from the atmosphere, and are emitted from (1) combustion of coal and oil, (2) cement production, (3) production of nonferrous metals and steel, (4) gold production, (5) waste incineration, and (6) Hg production.

Furthermore, fungicides and seed dressings (both have not been used for over 20 years), as well as sewage sludge used for soil amendment are serious Hg sources. Concentration of Hg in sewage sludge of the EU countries is reported to range from 0.6 to 3.0 mg/kg, and average 1.62 mg/kg (Mukherjee et al., 2004). Besides, fly ash used for land reclamation may elevate the Hg contents in soil (Mukherjee et al., 2007).

The highest Hg accumulation is reported for soils in the vicinities of Au and Hg mining or ore deposits and of chlor-alkali plants. Increased levels of Hg are also observed around coal power stations and metallurgic plants. In Poland, Hg contents of surface soils in such areas are up to 0.4 and 7.55 mg/kg, respectively.¹³⁹⁰ Extremely high concentrations of Hg were found in soils at a former battery recycling facility.¹³²⁶

Owing to the specific properties and behavior of Hg in soils, remediation of Hg-contaminated soils is complicated and costly. However, increasing Hg pollution in some regions, affected mainly

by Hg uses in the Au-amalgamation processes in Au mines, has stimulated intensive studies on this topic.¹²⁸⁴ During the Au–Hg amalgam processes, the mean total Hg losses of 1.32 kg are for 1 kg of Au produced.¹⁰⁸²

Over the past few decades, Hg has been used in the gold-amalgamation process in gold mines in Brazil (Amazon region) and in Siberian regions. The emission of Hg in one Hg mining area in central Brazil during the 1980s was estimated at about 80 t/year.¹⁴⁶⁷ The amount of Hg used for gold mining in Brazil increased from 50 t in 1985 to 5000 t in 1995. Yagolnister et al.¹⁵⁵⁹ estimated that 210 t Hg remain in the Siberian environment annually. Such amounts of Hg added to the environment create a great risk of its transfer to the food chain. An increased load of Hg is especially a serious threat in the Amazonian region due to specific climatic conditions in which Hg becomes extremely mobile. The impact of Hg released into the atmosphere and rivers, as well as on plants and soils, of both regions, was extensively investigated in recent years.^{1203,1284,1293,1559}

Although the physical sorption of Hg predominates in soils, in areas close to Hg ore deposits, sulfur compounds of Hg are frequently found.¹⁵¹³ The dredging of sediments could mobilize Hg in aquatic systems since dissolved oxygen increases the amount of Hg²⁺ and Me–Hg in solution.⁹⁴⁸ The soil pools of Hg and Me–Hg are the potential source of Hg accumulated in the freshwater food chain. Bishop and Lee (2004) observed high concentrations of Me–Hg (2–20 mg/kg) in stream-bank sphagnum mosses and (Me–Hg: 5–10 mg/kg) in swampy ground at a depth of 0–20 cm. Their study confirmed that the Me–Hg is not only from atmospheric sources but also from the methylation of inorganic Hg in soil water system, especially in wetlands. However, Wallschläger et al.¹⁵³⁶ have shown that only a small part (about 1%) of the total Hg present in contaminated soils can be mobilized by water, whereas most of Hg is fixed mainly by HA.

Serious environmental problem associated soil contamination with Hg as a possibility that a large amount of Me–Hg will result in its bioavailability. Thus, even simple Hg salts or metallic Hg create a hazard to plants and soil biota due the toxic nature of Me–Hg and Hg vapor. The volatilization of Hg from Hg-polluted soils can also have an adverse effect on human health when exceeding the EPA inhalation reference for Hg concentration established as 300 ng/m³ (Henry et al.¹³²⁶).

C PLANTS

1 Absorption and Transport

Plants seem to take up Hg easily from solution cultures (Figure 17.22). There is also much evidence that increasing soil Hg generally causes an increase in the Hg content of plants. The rate of increase of the Hg content in plants when the soil was the only source of this metal was reported to be highest for roots; however, leaves and grains also accumulated much Hg.^{321,481,748} These findings show that Hg is easily absorbed by root systems and is also translocated within plants. Blanton et al.,⁷⁹ on the contrary, reported that Hg levels in plants bear little relationship to its content of soils from a Hg mining district and that this reflects strong Hg bonds to soil components. Malikova et al.,¹³⁹⁷ however, stated that the Hg content of roots of *Artemisia* species is a function of its content in fine soil granulometric fraction (<0.1 mm) and increases up to 0.15 mg/kg at about 1 mg/kg Hg in this soil fraction.

Plants are known to directly absorb Hg vapor. Browne and Fang¹⁰⁷ reported that the rate of Hg vapor uptake is particularly influenced by illumination, but is unaffected by ambient temperature. Thus, soil Hg is not only directly absorbed by plants, but also indirectly absorbed from Hg vapor gradually released in soils. The soluble Hg forms in aerosols are easily adsorbed by pine needles and transported inside plants.¹³¹⁹

Lagerwerff^{247a} stated that Hg uptake by plant roots might be minimized by neutralizing the soil pH with lime. In addition, sulfur-containing compounds and rock phosphates are proposed to inactivate mercurial fungicides or elemental Hg in soils. Sorterberg,⁷⁴⁸ in contrast, reported that heavy liming was ineffective in reducing the toxic effects of Hg excesses in the soil. Furthermore, studies conducted by Oberländer and Roth¹¹⁰⁵ with labeled Hg (²⁰³Hg) showed that plants took up several times more Hg from the calcareous soil than from the acid one.

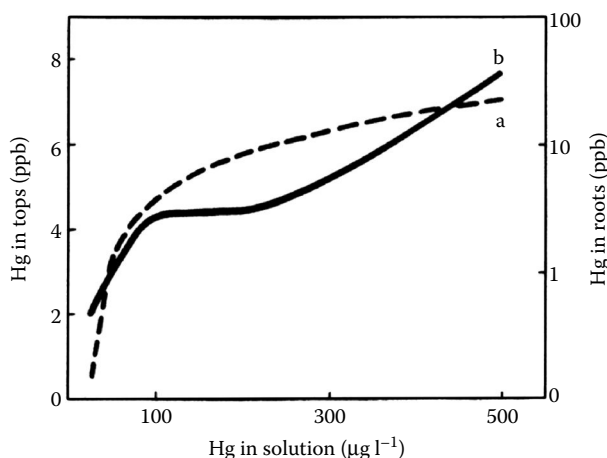


FIGURE 17.22 Uptake of Hg by 7-day-old oat seedlings from the culture solution of HgNO_3 concentration. (a) Tops; (b) roots. (Adapted from Skripnichenko J.J., Zolotaryeva B. N., *Agrokhimiya*, 9, 110, (Ru) 1980.)

Some transgenic plants (e.g., *Arabidopsis*) are very effective in the Hg volatilization (Watanabe, 1997). Rugh et al. (1996) suggested a molecular genetic approach to the transfer of Hg resistance genes to plant species as a potential means of phytovolatilization of Hg^0 . According to the authors, this technique may be useful to remove Hg from contaminated soils. In addition, it is possible to manipulate the transfer of Hg^0 in plants tissues to Hg^{2+} that may be another option for the Hg phytoremediation.

Translocation of Hg occurs between various plant tissues, for example, from: (1) apple leaves to fruits, (2) potato leaves to tubers, (3) rice leaves to grains, and (4) wheat and pea seeds treated with mercurial fungicides into the first-generation seed.^{447a} The content of Hg in rice grains harvested from plants treated with phenylmercuric acetate was reported to be the highest in bran; the fraction of Hg accumulated in whole grains apparently was associated mainly with gluten.³⁹⁵ The Hg content of grains is shown to be correlated with the ash content. The Hg content of bran is about 3 times higher, on average, than the Hg content of flour.¹¹⁰⁵

2 Biochemical Functions

Although Hg is strongly bound to amino acids of many proteins and enzymes, this metal seems to be relatively easily transported within plants. The Hg affinity to sulfhydryl groups apparently is the key reaction in disrupting metabolic processes of plants. Yathavakilla and Ceruso (2007) studied the Se–Hg interaction and observed that Hg was located in soybean roots in an association with Se in high-molecular-weight molecules.

Toxic effects in young barley were observed at the Hg level of 3 mg/kg, and its concentration of 0.01 mg/kg (AW) was reported to be severely toxic.^{171,710} The toxicity of volatilized elemental Hg and of some methylated compounds is known to be the most serious for plants. Siegel et al.¹¹⁴⁵ suggested that the Hg vapor accelerates senescence-related processes via elevated ethylene production and that the most active toxicant is elemental Hg, not ionic one. These authors found that young plants are more sensitive to Hg-saturated air than mature plants. Klope et al.¹⁰⁵² reported the retardation of growth of sensitive plant species at an Hg content ranging from 0.5 to 1 mg/kg, whereas Macnicol and Beckett¹⁰⁸¹ established the critical level of Hg from 1 to 8 mg/kg. Mhathre and Chaphekar¹⁰⁹² observed damage to plants even at 1 µg/L Hg concentration in the nutrient solution. The authors reported that Hg impact should be considered in events of failure of various metabolic processes like photosynthesis, chlorophyll manufacture, exchange of gases, and respiration. Antioxidative enzymes are reported to be more active under a relatively low of Hg levels in growth

media (Israr and Sahi, 2006). Moreover, Zhou et al. (2008) observed improved capacity of antioxidant enzymes in alfalfa treated with 40 μM HgCl_2 , but higher Hg concentration was toxic.

The symptoms of Hg toxicity are most commonly stunting of seedling growth and root development and inhibition of photosynthesis and, as a consequence, a reduction in yield. Hg accumulated in root tissue inhibits K^+ uptake by plants, although the stimulating effect of a low Hg concentration on K^+ uptake was also reported by Hendrix and Higinbotham.³¹⁵

The tolerance to Hg in higher plants also was reported, and although the mechanism of the physiological barrier is not known, it is most probably related to the inactivation of Hg at the membrane sites. The affinity of Hg to form insoluble compounds with S-rich proteins was reported for several plant species. Israr et al. (2006) observed that rattlebush (*Sesbania drummondii*) is able to accumulate and tolerate high concentrations of Hg; at above 100 mg/L of nutrient solution, the accumulation of Hg was 998 and 41,403 mg/kg in shoots and roots, respectively. Decrease in photosynthesis and activity of some enzymes was observed at these Hg concentrations. Particularly resistant to high Hg concentrations is the transgenic *Arabidopsis thaliana* with the genes for mercuric ion reductase (reduction of toxic Hg^{2+} to the relatively inert Hg^0).¹⁴⁰⁷ This plant (as probably others with such a gene) is believed to be useful as a phytoextractive plant to grow on the contaminated sites.

Some chemical fertilizers are known to affect the Hg uptake by roots. Their impact, however, differs with soil characteristics and amounts of Hg. Most commonly, ammonium sulfate and calcium phosphate decrease the Hg uptake by corn roots and increase the amount of Hg volatilizing from soil with high Hg contents.¹⁵⁵⁸

The resistance to Hg compounds in fungi and bacteria has received extensive studies. Weinberg⁸⁵⁶ reviewed results and demonstrated that in most cases the resistant strain was capable of volatilizing Hg. Plasmids are believed to carry determinants for the Hg resistance.

The biochemistry of Hg is associated mainly with biological transformation of its compounds. However, it is not clear yet which processes are the most important in its cycling in the environment. Doelman,⁹⁸² Jernelöv,³⁵⁹ Johansson et al.,¹⁰⁴¹ and Weinberg⁸⁵⁶ reviewed all topics related to the Hg transformation and to the Hg resistance in microorganisms. There is an assumption that microorganisms produce Me-Hg for the purpose of detoxifying the metal, but at the same time Me-Hg being readily absorbed through cell membranes is highly biotoxic.¹¹⁷¹

3 Concentrations in Plants

In general, Hg content of plants is high when the Hg content of soils is also high, but this relation does not always hold. Siegel et al.¹¹⁴⁷ discussed this problem and stated that several data support the hypothesis that specific local environmental factors strongly influence the accumulation of Hg in plants, even when the immediate soil concentrations are the same. Plants differ in their ability to take up Hg and can develop a tolerance to its high concentrations when grown in contaminated sites. Plants seem to absorb Hg easily from solution; however, there is not much evidence that increasing soil Hg generally causes an increase in the Hg content of plants, partly due to its great accumulation in roots. There is evidence, however, that increased Hg in roots may be translocated to the other parts of plants (Ferrara et al., 1991). Fine, hairy roots contain more Hg than coarse roots.

Increased Hg content in vegetations from contaminated sites indicates that it is taken up from soil; however, its atmospheric source is known to contribute significantly to Hg levels in plants as well. In recent years, attention has been paid to Hg uptake from the atmosphere. In some cases, the major part of Hg in the above-ground parts of trees seems to be associated mainly with its atmospheric deposition (Ericksen et al., 2003). Certain plant species, such as lichens, carrots, lettuce, and mushrooms, in particular, are likely to take up more Hg than other plants grown in the same sites (Falandysz et al., 2001, 2003). Besides, some parts of plants have a greater ability to absorb Hg, as in a case of apple flesh and apple pips (Table 17.13).

Indian mustard (*Brassica juncea* L.) reveals an ability to take up great amounts of Hg from contaminated soil. The highest Hg contents were in plants grown in soils with Hg at 1000 mg/kg (added

TABLE 17.12
Mercury in Food Plants Grown in Various Countries^a (μg/kg)

Plant	Range and Mean
Wheat, grains	<0.1–34
Barley, grains	1.1–34
Oats, grains	<0.1–22
Corn, grains	1.7–73
Lettuce, greenhouse	38.5
Tomato, greenhouse	22.0
Cucumber, greenhouse	7.7
Carrot	16.9
Potato	13.5
Apples	6.3
Spinach	68.5
Lemon	4.3 ^b
Tea, leaves	34–46
Leafy vegetables	64–139
Mushroom, caps ^c	630

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b At FW basis.

^c *Lecidum scrabum*, from the forest in Poland, after Falandysz and Bielawski 2007.

in the form of HgCl₂): 264–325 and 1775–2089 mg/kg, in shoots and roots, respectively, depending upon cultivars (Su et al., 2007).

The distribution of Hg in plants has recently received the most studies because of the Hg pathway into the food chain. Therefore, most information is at present related to the Hg content of plant foodstuffs. The background levels of Hg in vegetables and fruits vary from 2.6 to 86 and from 0.6 to 70 μg/kg (FW) (Table 17.12). Vegetables from western Siberia contain Hg within the range of 5–36 μg/kg (FW), and the highest concentrations were in cucumbers.¹²⁰³ Potato tubers collected in Poland contain Hg from 3 to 45 μg/kg (FW). The highest Hg concentrations were always found in crops grown in industrial regions.¹²⁴⁵ Shacklette et al.⁷¹⁰ reported Hg to range from 0.5 to 3.5 mg/kg in trees and shrubs from areas of Hg mineralization.

The Hg contents of cereal grains seem to be fairly similar for various countries and for certain kinds of cereals, with mean values ranging from < 0.1 to 34 μg/kg (Table 17.12). However, grain crops from land where mercuric compound dressings of seeds were used show some elevation (up to 170 μg/kg) in the Hg content.¹⁶² However, there also exists a report that using Hg in the United Kingdom for cereal seed treatments had very little effect on the Hg levels in grains.²¹⁴

Gracey and Stewart^{279a} reported Hg to average 39 μg/kg in alfalfa; Rovinskij et al.¹¹³⁰ gave the Hg range of 10–160 μg/kg (mean 50) in grasses of northern Kazakhstan. Other observations show that natural Hg levels in grasses and feed legumes do not exceed 100 μg/kg.¹⁰⁴⁵

Extremely high Hg content (from 72 to 200 mg/kg) was found by Lodenius and Herranen¹⁰⁷² in mushrooms (*Agaricus* species) that occur in the immediate vicinity of the chlor-alkali plant in Finland (Table 17.13). Nuorteva^{1104a} described a high accumulation of Hg by various species of mushrooms in Finland and gave the Hg range from 1.1 to 4.7 mg/kg for edible *Boletus edulis* growing in sites with no local pollution sources. Thus, mushrooms as well as rootless mosses and lichens are known to be suitable bioindicators for Hg in the ecosystems. Pine needles are also most often reported as sensitive Hg environmental biomonitors.⁹³¹

TABLE 17.13
Mercury Content of Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Part	Maximum or Range	Country	Reference
Mining area and metal-processing industry	Edible mushrooms	37.6	Yugoslavia	414
	<i>Boletus edulis</i>	0.3–1.5	Finland	1069
	Carrot, roots	0.5–0.8 ^a	Yugoslavia	116
	Apple, flesh	0.04–0.13 ^a	Yugoslavia	116
	Apple, pips	0.33–1.32 ^a	Yugoslavia	116
	Pine needles	0.2–11.4	Italy	931
Chloralkali or chemical works	Labrador tea, stems	1–3.5	U.S.	703
	Lettuce	0.09–0.35	Egypt	990
	Lettuce	0.15–0.36	Switzerland	637
	Spinach	0.11–0.59	Switzerland	637
	Corn, grains	0.074–0.136	Switzerland	637
	Radish, roots	0.032–0.29	Egypt	990
	Lettuce	0.1 ^a	Canada	776
	<i>Festuca rubra</i>	4.0	Great Britain	111
	Lichens	36.0	Finland	485
	Edible mushrooms	72–200	Finland	1072
Urban vicinity and parks	Edible mushrooms	33.6	Switzerland	635
	Bryophytes	1.4	U.S.	893
Sludged or irrigated farmland	Bromegrass	0.09–2.01 ^b	Canada	321
	Sudan grass	0.04–0.06	Hungary	1177
	Brown rice, grains	4.9	Japan	336
Application of fungicides or Hg salts	Potato, leaves	1.1–6.8	Canada	585
	Lettuce	0.1–0.3	Canada	496
	Oat, grains	0.63 ^b	Sweden	748
	Oat, straw	99 ^b	Sweden	748
	Wheat, grains	0.05–0.17 ^c	Poland	162
Volcanic areas	Lichens	0.102–0.213	Italy (Etna)	931
	Pine needles	0.007–0.027	Italy (Etna)	931
	Pine needles	0.031–0.330	U.S. (Hawaii)	931
	Horsetail	0.002–0.045	U.S. (Mt. St. Helens)	1146

^a FW basis.

^b Pot experiment.

^c After Hg treatment of seeds.

Several authors have made an attempt to estimate a permissible limit for Hg in food plants and have proposed 50 µg/kg (FW), whereas the background Hg levels for food plants was estimated by Kosta et al.⁴¹⁵ to range from 1 to 100 µg/kg. The EC Commission Regulation (2006) has not established the ML value for the Hg levels in food plants. The allowable limit of Hg in plant foodstuffs should always be calculated on the basis of daily Hg intake by a given population group.

18 Elements of Group 13 (Previously Group IIIa)

The Group 13 consists of five elements: boron (B), aluminum (Al), gallium (Ga), indium (In), and thallium (Tl). These elements have three electrons in their outer energy levels, thus their valence is mainly +3 (Table 18.1). Geochemical and biochemical properties, as well as the abundance in the biosphere, of all these elements are highly divergent. Their common characteristic is a strong affinity for oxygen. Among them, only B is metalloid (nonmetal) and plays a significant role in plants. Aluminum, being one of the basic constituents of the lithosphere, reveals amphoteric properties. Three other trace metals (Ga, In, and Tl) are widely, but at low concentrations, distributed in the lithosphere and biosphere.

I BORON

A INTRODUCTION

Boron is widely but not uniformly distributed in the environment and averages 15 mg/g in the Earth's crust (Tables 3.2 and 18.2). Its contents in igneous rocks range from 5 to 30 mg/kg and increases with the acidity of rocks. In sedimentary rocks its content is higher than in igneous rocks and is closely associated with the clay fraction. Its common minerals are: borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$; ulexite, $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$; kernite, $\text{Na}_2\text{B}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$; and tourmalines of a very complex composition. B might be associated with feldspars and micas. Its concentrations are elevated in carboniferous sediments and some coals.¹³⁵⁷ It is likely to be concentrated in fly ash, where its mean content is estimated as 509 mg/kg (Llorens et al., 2000). B has a high affinity for oxygen, due to which it occurs in the nature mainly as B–O compounds. Its chemical properties resemble that of Si.

The global B production in 2008 was 4.1 Mt (USDI, 2009). Borate deposits are quite rare and generally found in arid regions, with a history of volcanism or hydrothermal activities. B is a highly refractory metalloid and the production of pure B is rather difficult due to its high melting point and corrosive properties in the liquid form.

Borates have varied uses and the principal sector is fiberglass and heat resistant borosilicate glass. It is used in flame retardant tools and textiles, agricultural fertilizers and pesticides, cosmetics, antiseptics, and leather tanning. Its great proportion is added to laundry products. B and its compounds also have a special application in various military sectors and in organic syntheses.

B SOILS

Worldwide B average for soils is estimated as 42 mg/kg (Table 3.2). Its contents in various soil groups vary between 10 and 100 mg/kg, being enriched in Calcisols and Histosols, due to the preferential fixation by SOM (Table 18.2). Parent material is a basic source of B in soils as is indicated in Table 18.3. The largest quantities of B are accumulated in marine evaporates and marine argillaceous sediments; therefore B content can serve as a paleosalinity indicator. B elevated content in soils of solonetz complex is of a great concern (Azarenko, 2007). Levels of total B reported for soils of the United States seem to be fairly stable, with calculated means from 20 to 55 mg/kg^{219,706} High B contents, up to 1622 mg/kg (at average 65 mg/kg), are reported for some top soils of the Slovak Republic (Čurlík and Šefčík, 1999).

TABLE 18.1
Selected Properties of Trace Elements of Group 13

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C) (g/cm ³)	Valence ^b
B, boron	5	10.81	117	2.34	+3
Al, aluminum	13	26.98	143	2.69	+3
Ga, gallium	31	69.72	181	5.90	+1, +2, +3
In, indium	49	114.81	200	7.31	+1, +2, +3
Tl, thallium	81	204.38	208	11.84	+1 , +2, +3

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation states.

During chemical weathering of rocks, B goes easily into solution, forming several anions such as BO_2^- , $\text{B}_4\text{O}_7^{2-}$, H_2BO_3^- , and $\text{B}(\text{OH})_4^-$. Although B is likely to be retained by clays, illitic minerals in particular, and also by sesquioxides and organic substances, its concentration in soil solutions is relatively high, ranging from 67 to >3000 mg/l.¹³⁵⁷ The most common forms of B in the soil solution are, apparently, its undissociated acid, H_3BO_3 and partly $\text{B}(\text{OH})_4^-$. Only at pH > 7 other anions are likely to occur in soil solutions.

The behavior of B in soils was widely studied, and the basic results are summed up by Ellis and Knezek^{207a} and by Gupta.^{1320a} It was shown that B is sorbed more strongly by soils than other anions (e.g., Cl^- and NO_3^-), and the manner of B sorption by the clay surface is somewhat similar to that of cations rather than anions. B may be entrapped in the clay lattice by substitution for Al^{3+} and/or

TABLE 18.2
Abundance of Trace Elements of Group 13 in Rocks and Soils (mg/kg)

Rock/Soil	B	Al (%)	Ga	In	Tl
Earth's crust	15	8.2	15–19	0.25	0.85–1
Igneous rocks	—	—	—	—	—
Ultramafic	1–5	0.5–2	1–3	10–60	0.05–0.2
Mafic	2–20	7.3–8.8	15.24	0.02–0.22	0.1–1.4
Acid	10–30	6–8.2	16–20	0.04–0.20	0.6–1.8
Sedimentary rocks	—	—	—	—	—
Argillaceous	120–130	7–10	15–25	0.05–0.07	0.5–2
Sandstones	30–35	2.5–4.3	5–12	0.02	0.4–1
Calcareous	20–30	0.4–1.3	1–3	0.03	0.01–1.5
Soils ^a	42 ^b	1–5	15.2 ^b	0.06 ^b	0.5 ^b
Arenosols (sandy)	10–22	2–3.4 ^c	< 3–30	<0.2–0.5	0.014
Podzols (medium loamy)	10–35	—	5–50	0.03–4.1	0.18–2.8
Cambisols (heavy loamy)	15–40	—	5–70	—	—
Calcisols (calcareous)	10–100	—	5–30	—	—
Histosols (organic)	20–54	—	7–50	<0.1–2.6	0.17–0.22

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil average (Table 3.2).

^c Background values for various soils of Catalonia (Spain), after Tume et al. 2008a.

TABLE 18.3
Total and Water-Soluble Boron of Surface Soils in China^a (mg/kg)

Soil	Parent Material	Total B	Water-Soluble B
Acrisols	Granite	4–16	0.06–0.29
	Rhyolite	13–19	0.21–0.24
	Phyllite	15–40	0.02–0.19
	Red sandstone	25–28	<0.11
	Gneiss	13–22	<0.13
Different soils	Loess	55–87	0.14–0.70
	Quaternary red clay	48–96	0.08–0.37
	Limestone	49–145	0.14–0.34

^a After Zheng L., Zhu Q.-Q., Li-Hua T. 1980. *Acta Ped. Sin.* 17:228–239.

Si⁴⁻ (Krauskopf⁴²⁷). Thus, B-silicate compounds/minerals are likely to occur in soils. Adsorbed B on soil minerals is rather easily leachable; however, irreversibility of B sorption is observed. The variable fixation of B is due to different mechanisms of B-anion sorption, including ligand exchange, formation of surface complexes, and incorporation into clay mineral lattices.

In general, retention of B is greater on sesquioxides than on clay minerals, and the hydrous oxide of Al is more effective than that of Fe. Lindsay⁴⁷⁵ stated that the B adsorption on oxides of Fe and Al is believed to be an important mechanism governing the B solubility in soils. Cumakov⁹⁷³ observed a decrease in the solubility of B in soils heavily fertilized with K. This might be a secondary effect of the B affinity to illites and/or K-montmorillonites, which are known to be formed in soils enriched in K. OM also has an influence on the B mobility and availability, particularly in acid soils.¹⁶⁶ SOM adsorbs more B than mineral soil constituents. B sorption by HA increases with increasing pH, up to a maximum near pH 9, and decreases at pH > 9. Ligand exchange is a possible mechanism for the B sorption by OM. The B sorption capacity of DOM (294–333 mg/kg) is less than that of HA (589–2236 mg/kg); B-DOM complexes do not interact with soil components and may reduce the B toxicity (Communar and Keren, 2008).

Mechanisms of the B fixation that are likely to predominate in acid and neutral soils are: (1) oxy and hydroxy bonds, (2) surface coatings, and (3) incorporation into interlayer or structural positions of aluminosilicates. Jin et al.¹⁰⁴⁰ found the highest amount of B occluded in crystalline Al and Fe oxyhydroxides (up to 74% of the total soil B), and a smaller amount occluded in amorphous Al and Fe oxyhydroxides (up to 34%). On the contrary, in arid-zone soils, B is likely to be coprecipitated with Mg and Ca hydroxides as coatings of soil particles, and may also occur as Na-metaborate. In sodic soils, tourmaline is reported to be the major form and source of B.⁷²

In soils, B is considered to be the most mobile element among the micronutrients, although its water-soluble fraction is relatively low and varies from 3.2 to 5.3% of the total content.⁹⁷³ However, this B fraction highly varies upon soil parameters (Table 18.3). Nevertheless, B movement in soils follows the water flux, and in cool humid-zone soils B is leached downward soil profiles, whereas in soils of warm humid, or arid and semiarid regions, B is likely to concentrate in surface layers (Table 3.9). B may also be concentrated in other soil horizons that are enriched in illitic clays or sesquioxides (Figure 18.1).

Although B is rather a deficient micronutrient in most soils, some soils of arid or semiarid regions and soils overfertilized with B may contain hazardous amounts of this element. Some sewage sludge and fly-ash may also be significant sources of B contamination of soils. Waters discharged from coal mines and surface waters contaminated with B create agricultural problems in some regions, especially when they are used for the irrigation (Nicholson and Wood,¹⁴⁴⁰ Craw et al., 2006).

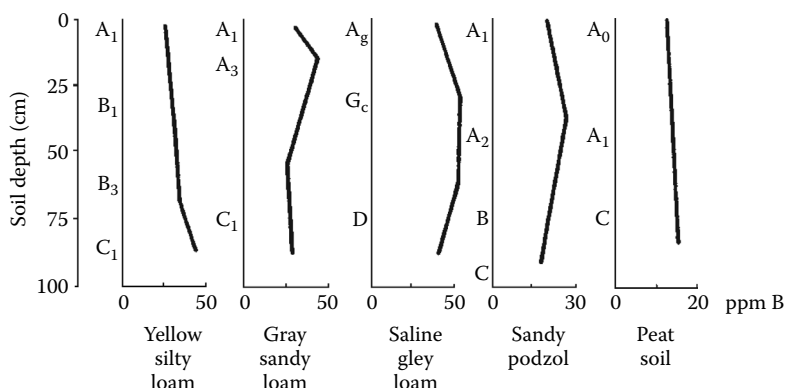


FIGURE 18.1 Distribution of B in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

Lucho-Constantino et al. (2005) observed increased B concentration in soils, up to 124 mg/kg, with the irrigation time.

Toxic B contents are primarily associated with solonetz soils (some developed on marine argillaceous sediments) and with man-induced contamination. The amelioration of high-B soils is very difficult.¹⁴⁴⁰ Light acid soils with a high level of B are easily improved by irrigation. The B hazard in sodic soils is proposed by Bhumbra and Chhabra⁷² to be ameliorated by the addition of gypsum, which converts readily soluble Na-metaborate to sparingly soluble Ca-metaborate. Also (Azarenko, 2007) reported that the application of gypsum and phosphogypsum reduces the degree of B salinization and its uptake by plants.

The phytoamelioration has been recently reviewed as a promising practice. B-tolerant grass species, and some *Brassica* species in particular, are suitable for the phytoremediation, because these plants can extract B from soils and decrease soil total B by about 7% compared with the control. According to McGrath,¹⁴⁰⁷ such a decrease, especially in extractable and leachable species of B in soils, can alleviate two problems: toxicity to subsequent crops and the potential toxicity of drainage water. Heavy applications of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ also resulted in a lower availability of B, especially in acid soils. As Prather⁶²⁶ reported, sulfuric acid can effectively aid in reclaiming soil high in B, however, the enhanced desorption of B by silicate ions is believed to be the main soil reaction.

C PLANTS

Boron is an essential element needed for the growth and development of plants (vascular, fungi, and bacteria). However, there are also reports that B is not essential for some fungi and algae, although it stimulates the N fixation by bacteria.^{504,630}

Its deficiency in crop plants is widespread. On the other hand, in arid and semiarid (especially irrigated) regions the B toxicity does also occur.

1 Absorption and Transport

Soluble forms of B are easily available to plants which can take up as undissociated boric acid as well as other B species present in the ambient solution. The property of boric acid to complex with polysaccharides is believed to play an important role in passive sorption.⁵³¹

There is still controversy as to the extent to which the uptake process is either passive or active. From several reviews presented by Moore,⁵⁴⁸ Price et al.,⁶³⁰ Shkolnik,⁷¹⁹ and Loneragan,⁴⁸⁹ it may be concluded that B uptake by roots consists of different phases. Moore⁵⁴⁸ described three processes, whereas Bowen⁹⁵ observed six phases of B absorption by barley roots. The metabolically controlled

process seems to be relatively minor; the B absorption mainly follows water flow through the roots. The B uptake is, therefore, proportional to its concentration and to the water flow. Indeed, Jin et al.¹⁰⁴⁰ reported that B concentration in corn tissues correlates positively with four easily soluble species of B, for example, water soluble, sorbed (either specifically or nonspecifically), and occluded in Mn oxyhydroxides. The sum of these four B species accounts for only 0.4 to 2.0% of the total B in soils. Szabo¹¹⁵⁸ reported that the B uptake by plants increases with its content of nutrient solution, and that is far greater than physiological needs. A relatively close relationship was observed between citrus leaf B and hot-water-soluble B in soil.

Hu and Brown¹³³⁷ reviewed the mechanisms of B absorption by plant roots; B is absorbed from soil solution mainly as undissociated boric acid, which theoretically should be membrane permeable. Also Kot (2009), basing on data published on the B phytoavailability, concluded that species differences in the B uptake are mainly due to variability in membrane permeability to boric acid, that is the main B species absorbed by plants. Thus, it can be predicted that B absorption is primarily determined by the B concentration in the nutrient solution and the transpiration rate of plants. However, B uptake differs between species, genotypes, etc. Also, the range of genotypic variation in plant response to a low B level in soil is very large. The B uptake in higher plants is most probably a passive process related to the external boric acid concentration and to the transpiration rates, but it is under the control of membrane permeability and internal complex formation. There is ample evidence that B nutrition has marked effects on the proton secretion and creation of an electrical potential gradient across the membranes. Thus, the B supply may stimulate proton-pumping activity of membranes, resulting in an increased driving force for ion influx (uptake). On the other hand, B deficiency results in an increase in membrane permeability of leaf cells. As compared with B-sufficient leaves (of sunflower), B-deficient leaves net efflux was 35-fold higher for K⁺, 45-fold higher for sucrose, and 7-fold higher for phenolic and amino acids.¹²⁴⁸

The water-soluble B pool is readily available to plants (Xu et al., 2001). The critical level for various plants is established for B-water soluble in soils as 0.5 mg/kg. However, for some legumes (e.g., lentils) a bit lower value, 0.4 mg/kg, is given for hot-water soluble B (Mahler and Shafii, 2007). Azarenko (2007) emphasized that the Ca:B ratio control plant reaction to B levels in growth media.

Brown and Shelp (1997) have classified plants into two categories: (1) species with restricted B mobility, and (2) species with significant B mobility. In the former case, water is the translocation agent for the B movement. The B uptake is therefore proportional to its concentration and the water flow. In the second case, B shows rapid and significant phloem mobility in species for which sorbitol is the primary photosynthetic product (Brown and Hu, 1996).

Soil pH is one of the most important factors affecting the B availability to plants. The lowest ratio of B uptake occurs when the soil pH is approximately 7. In alkaline soils, the availability of B increases with an increase in pH. This affects B hazard problems, particularly in irrigated saline-alkaline soils. The B absorption is temperature dependent and increases during warm periods. HA is reported to increase the B uptake by plants and thus is proposed to be added to enhance B-phytoremediation effects (Angin et al., 2008).

Boron is relatively immobile in plants; but because it is translocated mainly through the xylem, it is largely accumulated in old leaves in which the highest B content is in tips and margins.¹¹⁵⁸ Epigeal parts of plants usually contain more B than do roots. Although B is easily retranslocated in phloem, the B mobility in plant tissues is restricted. This phenomenon has implications in the diagnosis of the B imbalance in crops. The foliar application of B has not been widely used in agriculture as it was believed that the immobility of B would limit its effectiveness. Recent findings, however, shown that foliar application of B can supply B to flower and fruit tissues, and at any time to functional leaves. However, after foliar B fertilization, there was no corresponding effect on fruit yield (orange juice) or on chemical characteristics.¹²³²

Van Goor^{820a} compared B concentrations in phloem exudate (10 mg/kg) and in leaf tissue (34 mg/kg) and showed that B content is higher relative to other micronutrients. This may indicate

that the B absorption during its transport within veins is less than that of other elements. Although B may become quite immobile within plant tissues, there are indications that B can be transported from leaves to developing fruits and seeds.

2 Biochemical Functions

Despite of the essentiality of B for plants, its biochemical role is still not well understood. It has a complexing ability to trigger the movement of sugars and other materials, and it is involved in biological membrane bindings, conversion of glucose-1-phosphate sugars to starch, and in the metabolism of nucleic acids.¹²⁴⁸ It is believed that B plays the most significant role in the translocation of sugars because the borate-polyhydric complex is more mobile than polar sugar molecules. Most studies were done on the B effects on the metabolism of sugar beet, and it was shown that adequate B supply is necessary for the sugar synthesis (Figure 18.2).

The B deficiency in crop plants affects seed yield reduction, low male fertility, impaired reproduction, and disruption of the ascorbate metabolism.¹²⁷⁷ Its deficiency can be detected visually in dicots, maize, and wheat, at tissue concentrations of less than 20–30, 10–20, and 10 mg/kg, respectively.^{1320a} The B deficiency often occurs in plants growing in sandy soils because of its low availability. One of the causes of its deficiency in plants is dry soil that resulted in a low B mobility.

The physiological role of B differs from other micronutrients since this anion has not been identified as a component of any specific enzyme. Despite the essentiality of B for higher plants, the biochemical role of this element is still not well-understood. There have been many physiological experiments, usually with B-deficient plants, and the results are extensively reviewed by Price et al.,⁶³⁰ Shkolnik,⁷¹⁹ Jackson and Chapman,³⁴⁸ and Mengel and Kirkby.⁵³¹

Crop responses to B are highly variable on plant species and genotypes, as well as on growth conditions. Recent research on the B biochemistry emphasized the particular importance of B interactions with biological membranes, and with a variety of biomolecules. The deficiency of B in the field reveals an impaired sexual reproduction, marked seed yield reduction, and low male fertility. The boric acid is most probably involved in linking of some cell components.¹⁴⁰³ However, there is a great diversity of effects of a low B level on reproductive growth among species. As Dell and Huang¹²⁷⁵ stated, much of the data on severely B-deficient plants require reevaluation. However, positive responses to the B application was reported in over 80 countries, where soil parent material and texture are major factors controlling the B status of soils.

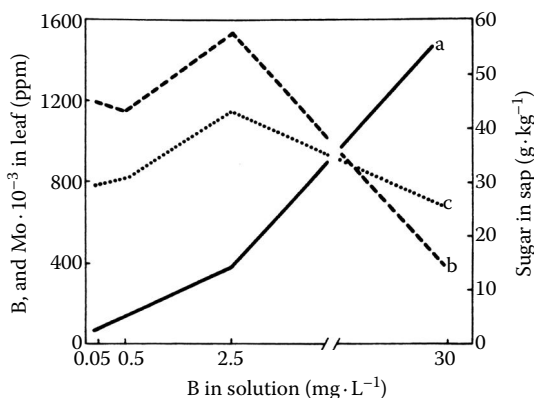


FIGURE 18.2 The effect on sugar beet of B levels in the nutrient solution. (a) B concentration in leaves; (b) Mo concentration in leaves; (c) sugar content of sap. (From Bonilla, I., Cadania, C., and Carpena, O., *Plant Soil*, 57, 3, 1980. With permission.)

The functions of B are related to some basic processes such as:

- Carbohydrate metabolism and transport of sugars through membranes
- Nucleic acids (DNA and RNA) and phytohormone syntheses
- Structural integrity of plasma membrane (boric acid is most probably involved in linking of some cell components)
- Tissue development (involvement in a messenger role in plants is suggested)
- Formation of stable complexes with compounds having *cis*-hydroxyl groups
- Formation of B complexes with the constituents of cell walls and plasma membranes

The B deficiency, especially in some commercial crops such as sugar beet, celery, sunflower, legumes, and apples is of a great agronomic concern. Specific symptoms of the B deficiency first appear as retarded and abnormal development of growing points, blue-green color of young leaves, and impairment of fruit formation (Table 5.8). Jackson and Chapman³⁴⁸ described that there is a general similarity of B deficiency symptoms and the response of plant tissue to treatment with growth hormones (e.g., auxin, gibberellic acid). Cakmak and Römheld¹²⁴⁸ reported that the enhancement in the concentration of phenolics in B-deficient tissues is a result of either stimulation of the pentose phosphate pathway or restriction in biosynthesis of phenolic alcohols. This is less pronounced in monocots as compared with the dicotyledons. Also, the concentration of ascorbic acid is reported to be substantially decreased in plant tissues in response to the B deficiency.¹³⁹³ Apparently, the biosynthesis of ascorbic acid was reduced and the oxidation of ascorbic acid was stimulated during B deficiency. In return, B fertilization (potato experiment) increases the concentration of ascorbic acid in plant tissues.¹²⁴⁸ In B-deficient leaves, impaired photosynthesis and enhanced phenol oxidation is associated with photooxidative damage to membrane and chlorophyll. B is required to detoxify the phenolics produced at higher light intensities, which can increase plant sensitivity to B deficiency. Diagnosis and prediction of the B deficiency for plant production was widely reviewed by Bell.¹²²⁰ The author emphasizes that one of the major difficulties with B deficiency diagnosis is that environmental factors such as low soil water, low temperature, high light, and low vapor pressure can induce a temporary B deficiency.

Bonilla et al.^{1235a} reported that nodules from plants (*Phaseolus vulgaris*) grown without B in the nutrient solution were smaller and had lower weights than controls. Thus, B is an obligatory requirement for normal nodule development and functioning. A great difference (3- to 10-fold) is observed in the root B-adsorption capacity between dicots and graminaceous monocots. Hu and Brown¹³³⁷ suggested that more B is required by dicots than graminaceous monocots because of a higher pectin content in the dicots. Mycorrhizal plants have a greater need for a B supply than do nonmycorrhizal plants.⁴⁵⁷ The beneficial impact of B on the nodule formation and nitrogenase activity in pea roots is reported by Bolanos et al.¹²³⁴ Dixon¹²⁷⁷ indicated a beneficial effect of B on the resistance mechanism of *Brassicas* against clubroot (*Plasmodiophora brassicae*), a soil-borne fungi pathogen that affects crops on a worldwide scale.

The assessment of B availability and its requirement by plants was extensively studied and it was found that analysis of water-soluble B in soils and plant tissue tests are adequate for the diagnosis and prediction of the B deficiency (Table 5.7).

Some plant species have a low B requirement and may also be sensitive to elevated B levels even only slightly above those needed for a normal growth. Therefore, toxic effects of B are likely to arise by excessive use of B fertilizers. The toxicity is usually more common in arid and semi-arid regions on soils with naturally high levels of B. Sensitive crop plants (e.g., cereals, cotton) may be affected by the B concentration in soil solutions as low as 1 mg/L, but 5 m/L may be tolerated by various plant species, whereas 10 to 15 mg/L is toxic to tolerant plants.^{11,90,648} The increased B content of irrigation water may be especially toxic to crops grown in an arid region.^{133,674} If there is an excess of B, a very high concentration (1000–1500 mg/kg) of this element often occurs in leaf tips or margins. These parts of leaves become necrotic, while at the early stage of

B toxicity the leaves are dark green and wilted. The growing points of such plants become dark and decay.

There is a narrow range of toxic and deficient B levels to plants. However, due to a great species variation, toxic symptoms are observed at very different B concentrations in plant tissues. For example, the B toxicity occurs in cotton at tissue concentrations of 422 mg/kg and in kenaf (*Hibiscus cannabinus*) at 222 mg/kg; both plants were grown in soil with 45 mg/kg B content.¹⁴⁰⁷ For animal nutrition, B levels above 150 mg/kg in fodder is not recommended.

3 Interactions with Other Elements

Interactions of B in the uptake of other nutrients by plants are apparently related to changes in membrane permeability and in the status of cell colloids. Physiological mechanisms of these reactions are, however, still not well-understood.

Several interactions reported for B and other trace elements, as shown in Figure 5.8, have not yet been confirmed. The possible antagonisms with Cu, Cr, Mo, and Mn may be effects of indirect influence through the increase of growth, hence increased demands for a given micronutrient. However, Lambert et al.⁴⁵⁷ reported that B-deficient alfalfa also contained a lower amount of Cu. Leal et al.⁴⁶³ explained the Fe–B antagonism as a result of increased B accumulation in roots with a higher soil supply of Fe. Graham et al.¹⁰¹³ demonstrated that both low Zn and high P supplies increase the B accumulation in barley plants. Thus, the B uptake to toxic levels in plants may be expected in soils with a low level of available Zn, a high B level in rooting zones, and a high P fertilization rate. Findings of these authors show that at the excessive B concentration, the toxicity symptoms first appeared on low-Zn plants, which suggests a partial protective effect of Zn against toxic levels of B in rooting zones.

The B–Si antagonism is an effect of possible competition by silicate ions for adsorption sites of B, and this reaction was observed in both soil environments and root tissues.

The B–Ca interrelationship is reported most often. Plants grow normally at a certain balance in the intake and in tissue concentrations of Ca and B. Lime-induced B deficiency has frequently been observed in acid soils. However, it has also been shown that at equivalent amounts of Ca, tissue B concentrations are much higher when CaSO₄, rather than CaCO₃, is applied to a soil.^{626,772} Liming is believed to result in the decreased B adsorption; thus, toxic effects of B may be reduced or prevented by adding Ca to soils. These phenomena have been ascribed to both reactions within soil media and metabolic processes.

The B–P interactions in soils are related to the interference of P ions with the B mobility. B and P have similar reactions with OH[−] groups; thus, the uptake of these elements by plants is likely to follow similar patterns.⁵² The uptake and distribution of P are reported to be dependent on B concentrations because B increases P immobilization in roots.⁴⁶³ Graham et al.¹⁰¹³ described that interactions between P and B are not yet fully understood, however, these two elements influence the integrity of cell membranes, and imbalances in these nutrients could lead to aberrations in the ion uptake.

Other effects of other nutrients, such as K and N, on the B content of plants are, presumably, secondary results of increased plant growth or of some physiological disorders. B is reported to have beneficial effects on the Al toxicity to plant growth. However, the ameliorative effect of B is related rather to root activity under Al stress, and not directly to Al toxicity involved in the ascorbate metabolism.¹³⁹³

4 Concentrations in Plants

The B contents of plants grown under natural conditions widely vary for plant species (Table 18.4). The lowest B contents is always in seeds and grains, and the highest (>100 mg/kg), in sugar beet and legumes leaves (Figure 18.3).

TABLE 18.4
Boron in Food Plants Grown in
Various Countries^a (mg/kg)

Plant	Mean
Wheat, grains ^b	0.69
Barley, grains ^b	0.83
Rye, grains	4.3
Oats, grains	3.1
Bean, pods	13
Cabbage, leaves	14
Carrot, roots	9.9
Onion, bulbs	10
Potato, tubers	6
Tomato, fruits	6
Apple, fruits	8.3
Orange, fruits	8.4

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b After Eriksson (2001).

The B contents of plants grown under natural conditions widely vary for plant species and kinds of soil. In general, however, dicot plants have a higher B requirement and thus a higher B content than do monocot plants. The average B content of forage plants from various countries supports this statement (Table 18.5). The average B concentration in grasses is 5.7 mg/kg, whereas the content of alfalfa and clover is 37 mg/kg. On the basis of these values, the ratio of B in dicots to monocots is 6.5, which is higher than that calculated by other authors.¹⁶⁶ Shacklette et al.⁷¹⁰ reported that trees and shrubs (B content: 50–500 mg/kg AW) generally contain 2 to 10 times as much B as do vegetables.

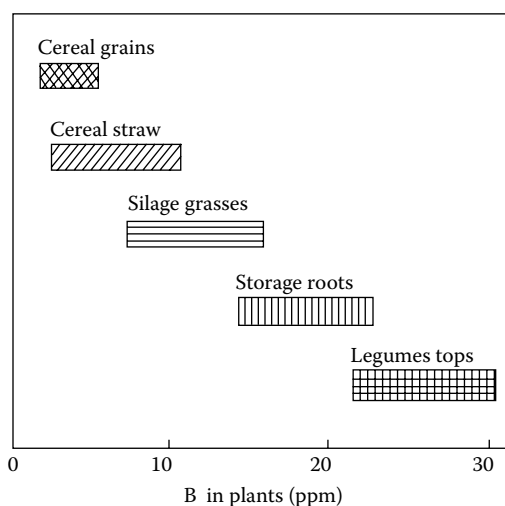


FIGURE 18.3 Distribution pattern of B in different crop plants. (Modified from Ylärinta, T. and Sillanpää, M., *Ann. Agric. Fenn.*, 23, 158, 1984.)

TABLE 18.5
Boron Content of Grasses and Legumes (mg/kg)

Country	Grasses		Clovers		Reference
	Range	Mean	Range	Mean	
Great Britain	—	26 ^a	—	—	112
Czech Republic	14–30	22 ^a	—	—	154
Finland	3.9–6.3	4.9	—	—	590
Germany	—	—	20–50 ^b	—	65
	—	—	20–60	—	65
	—	—	30–100 ^b	—	65
Hungary	1.0–7.9	5.8	20–35	33	803, 804
Japan	1.6–12	4.9	12–35	21	770
Poland	1.0–15.6	5.6	11.3–16.5	14	1045
New Zealand	1.7–10.0	5.2	6–120	26 ^b	865
U.S.	<5–20	7.4	10–70	22 ^c	710
Russia	2–10	5	32–50	40 ^b	337
	—	—	10–40	26	337

^a Pasture herbs.

^b Alfalfa.

^c Calculated from AW basis.

The critical B levels for most plants range at 5–30 mg/kg.¹³⁵⁷ The toxic B contents are reported by various authors as follows (in mg/kg): (1) John et al.³⁶² reported spinach reduced yield at levels of 348–990, whereas corn could tolerate the content of 1007–4800; (2) Chapman¹³¹ reported toxic concentrations for alfalfa to be from 283 to 333; (3) Alikhanova¹¹ observed the B toxicity in cotton at 283–333 concentration; and (4) Davis et al.¹⁷¹ stated that B is toxic to barley seedlings at content of 80.

Cole crops are known to be very resistant to high B concentrations in plant tissues. Gupta et al.¹⁰²⁰ found the B levels as high as 123 and 161 mg/kg in brussels sprouts growing in soils with 7.6 and 91 mg/kg B (hot water soluble), respectively, and no symptoms of toxicity were observed. Ryegrass grown in a soil amended with fly-ash (enriched in easily soluble B) contained up to 430 mg/kg B and did not show toxic symptoms.¹⁰⁴⁵ In orchards where citrus trees showed some toxicity symptoms, about 14% of leaf samples had B greater than 200 mg/kg, and only 18% had B less than 100 mg/kg.¹²¹⁰

The B toxicity in some crops (commonly in cereals and sunflower) occurs most often on soil contaminated with B due to: (1) irrigation with treated municipal wastewaters or with B-enriched river waters in arid climatic zones, (2) amendment with fly-ash, and (3) foliar application of B on citrus and/or apple orchards. Especially, MSW and coal fly ash composted together are a source of available B affected plant tissue-B increase and negative growth effects of some vegetables (Brinton et al., 2008). In plants grown in saline soils, foliar levels of B may be reduced because high soil salinity reduces plant water uptake.¹²⁹⁹ Plants that exhibit salt tolerance are usually also sufficiently tolerant of B elevated concentrations in growth media.¹⁴⁵⁰

Recently, B has been considered as a widespread environmental contaminant and thus phytomanagement of B-contaminated sites has been investigated. Leaves of poplar (*Populus* sp.) grown in a substrate containing 30 mg/kg B absorbed this element up to the concentration of 845 mg/kg, whereas stems contained 21 mg/kg (Robinson et al., 2007). A great capability to accumulate B from polluted waters, up to 1900 mg/kg, reveals duckweed (*Lemna gibba*) (Marin and Oron, 2007).

II ALUMINUM

A INTRODUCTION

Aluminum is the third most abundant element in the Earth's crust, occurring at about 8% (Table 18.2). It has only one oxidation state +3 (Table 18.1), reveals lithophile properties, and is slightly mobile in hypergenic zones. However, in acidic environments, its solubility increases and Al becomes toxic to terrestrial and aquatic species. Due to its amphoteric character, Al reacts with acids and strong alkalis. It exhibits a strong relation to electronegative groups (e.g., OH⁻) and to some ions (e.g., F⁻).

Aluminum is either a main or secondary component of many minerals, especially of all silicates. Minerals composed only of Al are: boehmite, γ -AlOOH; diaspore, α -AlOOH; corundum, Al₂O₃; and hydrargilite/gibbsite, γ -Al(OH)₃, that is the main component of bauxite rocks. Host minerals of Al are: feldspars, micas, and all layer silicates.

The world production of Al in 2008 was 39.7 Mt. Al recovered from purchased scrap was about 3.6 Mt, of which about 60% was from new scrap and 40% from old scrap (USDI, 2009). Uses and recycling of Al has become a serious environmental concern. Several recommendations are given in the LCA programs (Frees, 2008).

Due to versatile properties of Al, it is used in different industrial sectors including: metallurgical, packaging, transportation, construction, and electrical and chemical productions. Its compounds are used in paper manufacturing, water purification, sugar refining, wood preservation, leather tanning, waterproofing textiles, and many others. It is also used as a corrosion inhibitor, cement accelerator, and has several others applications.

In the 1970s and 80s, forest began to die due to tree-root damage in Europe, the United States, and Canada which was found to be due to acid rain that mobilized metals in soils, especially Al. Nuorteva (1990) assessed forest damage to be due to a high Al-induced Ca deficiency syndrome. However, Freda (1991) described the Al toxicity as a complex phenomenon which is influenced by the hardness, pH, and DOC of waters.

B SOILS

During weathering of primary rock minerals the series of Al hydroxides of variable charge and composition, from Al(OH)²⁺ to Al(OH)₆³⁺, are formed and they become structural components of clay minerals. The only stable and frequently occurring ion, Al³⁺, is known to coordinate with oxygen-bearing ligands. Some Al silicates (e.g., imogolite) are believed to be the principal dissolved Al species in Podzols, while in some sulfate- and acid-spoiled soils, the Al solubility is governed mainly by Al sulfate.¹¹⁰² In general, the solubility of Al hydroxides is low, especially in the pH range of 5–8, and solubility decreases with aging. Freshly precipitated solid Al hydroxide species and colloidal species have a potential for anion adsorption, as well as the ability to flocculate negatively charged particles. Thus, Al hydroxides contribute greatly to various soil properties.

Depending on properties of environmental compartments, a variety of Al complexes and species can occur, as well as free Al(H₂O)₆³⁺, which is regarded as the most toxic to biota. According to Klöppel et al.¹³⁶⁶ Al products exposed to environmental media, do not increase significantly toxic Al species.

Aluminum ions in soil solutions depend on the pH and predominates within various pH ranges:

- Al³⁺ at pH 4–5
- Al(OH)²⁺ and Al(OH)₂⁺ at pH 5.5–7
- Al(OH)₄⁻ at pH 7–8

Organic compounds, both high and low molecular weight (e.g., HA, citric acid), decrease soil acidity and therefore decrease free Al ion contents. Al is known to form several polynuclear species in aqueous environments. The tridecameric (Al₁₃) species, AlO₄Al₁₂(OH)₂₄(H₂O)₁₂⁷⁺, is the primary

proposed model of polynuclear species in soil-water systems. The Al_{13} polynuclear species is believed to be important in the behavior of Al in soils and aquatic systems, and is known to reveal a complexing ability to immobilize some free cations.¹²¹¹ Berth and Parker¹²²⁴ reported that polynuclear Al_{13} and Al-montmorillonite immobilize Cd and Zn in polluted soils. The binding of Zn and Pb by montmorillonite is stimulated by Al hydroxides and low-molecular-weight acids.¹³⁴⁴

The total Al content of soils is inherited from parent rocks; however, only that fraction of Al which is easily mobile and exchangeable plays an important role in soil properties.⁵²⁸ In acid soils with $pH < 5.5$, the mobility of Al increases sharply and very actively competes with other cations for exchange sites. A sudden increase of the Al solubility is observed mainly in the narrow pH range from 4.5 to 4.0. The solutions of neutral soils contain Al at the order of about 400 $\mu g/L$, while in the soil solution at pH 4.4, Al concentration was reported to be 5700 $\mu g/L$.²⁷⁹ Nilsson and Bergkvist¹¹⁰² studied Al chemistry in a Swedish Podzols and found higher Al concentrations (ranging from 95 to 115 $\mu M/L$) in leachates collected below the B horizon than below the upper A_0 and A_2 horizons. These investigators emphasized a significant contribution of organic Al species to the Al mobility. They stated that DOC (probably FA) affects the Al release through the complex formation in the upper soil layer, while the other types of mechanisms are operating in the lower B horizon. Also, soil acidification due to the atmospheric deposition of S (mainly SO_2) increases the Al solubility in soils, possibly by the formation of soluble $Al(OH)SO_4$. With sulfides (e.g., pyrites) present in soils, oxidation produces H_2SO_4 , which interacts with other minerals to yield Al ions which then occupy exchange sites.¹¹¹⁸

C PLANTS

Aluminum is a common constituent of all plants and is reported to occur in higher plants in the range X0 to X00 mg/kg. However, contents of this element in plants vary greatly, depending on soil and plant factors (Table 18.6). Some species of Al-accumulating plants may contain Al more than 1000 mg/kg.

TABLE 18.6
Aluminum in Food and Forage
Plants^a (mg/kg)

Plant	Mean
Wheat, grains ^b	31
Barley, grains ^b	38
Rye, grains ^b	70
Oats, grains ^b	47
Cabbage, leaves	8.8
Spinach, leaves	104
Onion, bulbs	63
Potato, tubers	76
Tomato, fruits	20
Apple, fruits	7.2
Orange, fruits	15
Grasses	7–3410
Clovers	85–3470

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b Data for Poland, after Indeka and Karaczun (1993).

Physiological functions of Al in plants are not clear, although there is some evidence that low levels of Al can have a beneficial effect on plant growth, especially in Al-tolerant plant species.^{141,241} Small quantities of Al are believed to activate some enzymes and to control physical properties of plasma and membrane permeability. According to Ślaski,¹⁵⁰⁰ Al ions interact with root tips of cereals sensitive to an excess of Al in mobile forms. Roots of cereals tolerant to the Al excess (e.g., wheat, sp. *Atlas*) exclude phosphate compounds, increasing pH at the rhizosphere and complexing Al^{3+} ion, limiting its uptake.¹⁴⁵¹ The Al injury or toxicity is often reported for plants grown in acid soils. Several recent reviews were published on this subject and emphasized that a high availability of Al in acid soils is one of the limiting factors in the production of most field crops.^{44,241,646} In fact, the reduced yield of crops, as well as forest decline on acid soils is often due to increased availability of Al rather than high H^+ concentrations. The mobile Al in acid soils can be taken up rapidly by plants and it creates a problem of chemical stress in plants. Citrates excluded in the rhizosphere protect plants against increased Al uptake. However, in acid soils oxide minerals adsorb citrates and thus increase Al phytoavailability (Hashimoto, 2007). Foy⁹⁹⁸ reported that Al toxicity in subsoils is particularly harmful because it causes shallow rooting, drought susceptibility, and poor use of subsoil nutrients.

Plant species and even cultivars of the same species differ considerably in their ability to take up and translocate Al, depending on plant tolerance to the Al excesses. In most plants, the symptoms of Al injury first appear in roots, where it is likely to be accumulated. However, this is not necessarily associated with the Al tolerance.

Tea bushes grow mainly in acidic soils and therefore accumulate much Al. The median content of tea leaves from plantations of various countries is 2969 mg/kg.¹³³⁴ Chinese tea contains Al at levels from 676 to 1875 mg/kg, of which about 35% is extracted to hot water. Wong et al.¹⁵⁵⁰ reported that tea drinks contain Al within the range of 2.1–2.5 mg/L.

As Foy et al.²⁴¹ stated, the physiological mechanisms of Al toxicity are still debated, however, they are related mainly to impaired nutrient uptake and transport, and to an imbalanced ratio of cations to anions. The Al excess in plants is also likely to interfere with cell division and with properties of the protoplasm and cell walls. Al is known to form organic complexes and therefore to precipitate nucleic acids. Taylor^{161a} reviewed findings on Al phytotoxicity which is related to several effects, mainly to reductions in root elongation and root biomass production, reduction in membrane fluidity, and changes in DNA synthesis. The most significant mechanisms of Al tolerance depend upon: (1) exclusion of Al at the root–soil interface, (2) plant-induced pH barrier in the rhizosphere, (3) Al immobilization at cell walls and binding by proteins, and (4) evolution of enzymes.

The complex physiology of the Al toxicity in plants is reflected in several interactions with the uptake of nutrients such as P, Ca, Mg, K, and N. In general, cation uptake by plants is reduced with an excess of Al. The Al toxicity is also frequently associated with increased levels of Fe and Mn, and possibly other trace metals, which are readily available in acid soils. However, Al-induced chlorosis due to impaired Fe metabolism in some plants and Fe deficiency were also reported by Foy et al.²⁴¹ The Al excess in plants is known to induce Ca deficiency or reduce Ca transport. Also, the Mg content of plants is greatly decreased by Al, and this decrease in Mg may be an important response of plants sensitive to Al. The addition of both Ca and Mg to soil greatly reduces Al toxicity.

The interaction of Al and P is related to the formation of sparingly soluble Al phosphates in soils and to other coreactions of internal adsorption or precipitation of Al and P, as well as to Al interference with normal P metabolism, mainly in root tissues. Jarvis and Hatch¹⁰³⁶ observed that the effects of Al^{3+} at low concentrations were related to the reduced uptake of P and NO_3^- by white clover. Hence, Al toxicity is often manifested as a P deficiency, and P is an effective agent for detoxifying excess Al. Also Si is known to play a significant role in detoxifying Al.^{241,998}

The Al tolerance in plants seems to be associated with NH_4 tolerance because nitrification is strongly inhibited in acid soils. The mechanisms of the Al tolerance in plants are known to be genetically controlled; therefore, the selection of plants having genetic adaptability may be a solution to the problem of Al stress for crops grown in acid soils.^{241,998} The Al toxicity is one of the major growth-limiting factors in many acid soils.

III GALLIUM

A INTRODUCTION

Average Ga concentration in the Earth's crust vary within the range 15–19 mg/kg (Tables 3.2 and 18.2). Its contents in rocks range from 1 to 25 mg/kg, being the lowest in ultramafic and calcareous rocks. It increases in argillaceous sediments showing an association with clay minerals. The Ga valency is generally +3, but the oxidation states of +1 and +2 may also occur (Table 18.1).

The Ga geochemistry is similar to those of Al, but it is less reactive than Al. There are not many Ga minerals. Those containing above 30% of Ga are: gallite, CuGaS_2 ; sohngeite, $\text{Ga}(\text{OH})_3$; and tsungeite, $\text{GaO}(\text{OH})$. It may be associated with feldspars, amphiboles and micas, and may form different complexes with some anions (e.g., O, F, S). The electro-negativities and ionic potential suggest that Ga may be amphoteric.

The world Ga production was roughly estimated as 203 t in 2003 (USGS, 2004). It occurs in minute concentrations in some ores and is generally produced as a by-product of the production of Al from bauxite. Its level varies in bauxite mined from different regions, the highest concentration (0.08%) being reported for the bauxite from tropical regions. It is also obtained at sphalerite (ZnS) and other sulfide metals exploration.

The Ga reveals semi-conducting properties. Its primary uses are in electronic components, mainly as GaAs and GaN compounds. Due to its unusual properties of stability, it is applied in metal alloys being liquid at room temperature. Different Ga compounds are radiopharmaceuticals in medicine.

B SOILS

The average Ga content in soils is estimated as 15.2 mg/kg and its abundance varies from <3 to 70 mg/kg (Table 18.2). The Ga distribution in soils reflects a positive correlation with clay fraction, and Fe and Mn hydroxides. Due to the association of Ga with Al, its contents in soils exceed some times that of the continental crust. The Ga concentrations in soils of various countries are reported, as follows (in mg/kg): (1) 16–35, the United States, San Joachin Valley (Wilson et al., 1994); (2) 18–23, Japan (Takeda et al., 2004); (3) 3.4–16, Sweden (Eriksson, 2001); (4) 6–17, Russia (Gribovskaya et al.²⁸³); (5) 6–48, New Zealand (Wells⁸⁶³); and (6) 13, average, Slovak Republic (Čurlik and Šefčík, 1999).

Gallium is relatively slightly mobile in soils, partly due to a low solubility of $\text{Ga}(\text{OH})_3$, its common compound. Therefore, it might be a useful marker for the characterization of soil genesis. Welch et al. (2004) observed that during weathering Ga is preferentially mobilized compared to Al and is also mobilized by complexing organic compounds. In general, however, Ga is associated with Al minerals and positively correlates with the clay fraction. The distribution of Ga in soils also shows a relation to Fe and Mn oxides. Ga is likely to be accumulated in SOM and its higher concentrations are reported for bioliths, but whether Ga forms organometallic complexes has not been confirmed.⁸⁵⁵

Gallium is emitted from Al works and during coal combustion. Its elevated contents in effluents, sludge, and composts may be a source of soil contamination. Its increased levels are reported for some waste products in Denmark (EPA, 2003), as follows (in mg/kg):

- Waste water treatment plant, 2.2–6.4
- Household compost, 1.9
- Garden-waste compost, 1.6
- Motorway dust, 4.3–5.2

However, elevated concentrations of Ga in surface soils have not yet been reported. Asami et al.¹²⁰⁹ studied soils from both sites, polluted and unpolluted by metals in Japan, and did not notice any significant difference. Ga contents of both kinds of soils range between 13 and 16 mg/kg.

C PLANTS

There are insufficient evidences to demonstrate either the necessity for or the toxicity of Ga in plants, although some studies have suggested a beneficial role of this element in the growth of microorganisms and some fungi, such as *Aspergillus*. Nevertheless, Ga is commonly found in plant tissues, and its concentration is reported to range from 3 to 30 mg/kg (AW) in a variety of native species from the United States, as reported by Shacklette et al.,⁷¹⁰ and from 0.02 to 5.5 mg/kg in native herbage from Russia, as described by Gribovskaya et al.²⁸³ and Dvornikov et al.¹⁹⁹ The highest Ga contents were given (in mg/kg) by Wedepohl⁸⁵⁵ and Bowen⁹⁴ for lichens and bryophytes, 2.2–60, and 2.7–30, respectively. According to Berg and Steinnes,¹²²³ elevated Ga contents, up to 16 mg/kg, in moss sampled in Norway may reflect the atmospheric deposition.

IV INDIUM

A INTRODUCTION

Values given for the average In content in the Earth's crust are variable within the range from 0.11 to 0.25 (Tables 3.2 and 18.2). Its concentrations in igneous rocks, especially in ultramafic ones are higher than in sedimentary rocks.

The In oxidation state varies from +1 to +3. It is likely to precipitate under condition that form Fe and Mn hydroxides, and therefore is associated with Fe-bearing minerals. Due to chalcophilic properties, In forms sulfide minerals, such as: indite, FeInS_4 ; and roquésite, CuInS_2 . It is often associated with selenide and telluride minerals, as well as with sulfide minerals (e.g., sphalerite, ZnS ; galena, PbS ; chalcopyrite, CuFeS_2). Generally the In contents in these minerals vary between 10 and 20 mg/kg and they are its main sources for mining. However, it is often recovered from residues, slag, dusts, and ashes, during the production of Zn, Pb and Sn.

The In concentration up to 10% is found in some Fe oxides as a result of their sorption capacity. In acid solutions, the In may form several ionic species [e.g., InCl^{2+} and In(OH)^{2+}], which are precipitated in the pH range of 5–9. Above pH 9.5, the anion In(OH)_4^- is likely to occur. The In is commonly found in coals and crude oil and is reported to be combined with organic substances.

Estimated world production of In in 2008 was estimated as 568 t (USDI, 2009). About 60% is produced in China (<http://www.indexmundi.com/minerals>; accessed on March 15, 2009).

Indium is generally used in alloys, solders, and electronics. It is used for coating high speed bearings, transistors, and photoconductors. It is often used in low melting alloys and for thermal-neutron absorbers of nuclear reactors. In is also used in Na-lamps and its compounds have replaced Hg in alkaline batteries (EPA, 2003).

B SOILS

Worldwide soil In is estimated as 0.06 mg/kg, and it ranges in different soils from 0.03 to 0.5 mg/kg (Tables 3.2 and 18.2). During weathering, In is oxidized to In^{3+} , follows Fe^{3+} , Mn^{4+} , and partly, Al^{3+} , and usually precipitates under conditions which form hydrous Fe oxides. In soils, In seems to be associated with OM and therefore its concentration is increased in surface-soil horizons. Its contents in soils from different countries are reported as follows (in mg/kg):

- Japan: 0.08 to 0.1, in Acrisols and Cambisols, respectively (Takeda et al., 2004)
- Japan: soils from the vicinity of Zn–Pb smelter, 0.11–1.92 (Asami et al.¹²⁰⁹)
- Brazil: average, 0.15 (Fergusson, 1990)
- China, reference sample, 0.03 to 4.1, mean 0.68 (Govindaraju¹³¹³)
- Sweden: up to 0.06, average <0.04 (Eriksson, 2001)
- Sweden: surface horizon of forest soils, mean 0.007 (Tyler, 2005)
- U.S. <0.2–0.5, mean 0.2 (Chattopadhyay and Jervis¹³²)

The In distribution among soils indicates its association with clay fraction. It is also likely to be sorbed by Fe and Mn hydroxides. Soluble species of In in soils are mainly InCl^{2+} and In(OH)^{2+} that are mobile at acid and neutral pH range. Above pH 9.5, the anion In(OH)_4^- is likely to occur.

Elevated concentration, up to 4.2 mg/kg, of In is observed in soils near metal plants, especially Pb and Zn (Smith et al.⁷⁴²). Some sewage sludges may be a source of In.²⁴⁹ Increased contents of In are reported for waste water treatment plants (<0.09 mg/kg) and motorway dust (<0.07 mg/kg) (EPA, 2003).

C PLANTS

Although In is known to be readily available to plants, its accumulation in plants is not observed. Its common contents in plant tissues vary between 1 and 2 mg/kg. Physiological In effects on plants are reported mainly in relation to In-induced toxicity in roots that occurs in various plants at In concentrations in culture solutions from 1 to 2 mg/kg (Smith et al.⁷⁴²). Microorganisms reveal a greater resistance to In concentrations in solution than do higher plants. However, the In concentrations of 5–9 mg/kg were reported to inhibit activity of nitrate-forming bacteria in soil.

Few data on In in some plants are reported by Fergusson (1990), as follows (in $\mu\text{g/kg}$ FW): (1) beets, 80–300; (2) leaves of fruit trees, 0.64–1.8; (3) tomato leaves, 0.64–1.8; and (4) vegetables 30–710. Cereal grains sampled in Sweden contain In at <5 $\mu\text{g/kg}$ (Eriksson, 2001).

Beets grown in soil amended with sewage sludge contain much higher amounts of this metal, in the range of 80–300 $\mu\text{g/kg}$ (Furr et al.²⁴⁹). Unwashed grass samples from industrial regions contain In at the range of 8–2100 $\mu\text{g/kg}$ FW (Smith et al.⁷⁴²).

V THALLIUM

A INTRODUCTION

The Tl average content of the Earth's crust is estimated as 0.5 mg/kg or as the range of 0.85–1.0 mg/kg, depending upon data sources (Tables 3.2 and 18.2). Its content seems to increase with increasing acidity of igneous rocks and with increasing clay content of sedimentary rocks.

Thallium has lithiophilic properties and occurs in three oxidation states, but preferable in +1 (Table 18.1). It is associated with K-minerals (e.g., feldspars, micas) and with S-minerals (e.g., pyrite, sphalerite). It occurs in several minerals, but only in some it is present at higher amounts, for example: lorandite, TlAsS_2 ; and avicennite, Tl_2O_3 . Its other minerals, are rather rare and without any potential mining, such as: crookesite, $(\text{Cu,Tl,Ag})_2\text{Se}$; and hutchinsonite, $\text{Pb,TlAs}_5\text{S}_9$.

The global production of Tl in 2008 was 10 t (USDI, 2009). It is generally recovered during the production of Zn, and may be also obtained during the recovery of Au and U (Twidwell and Beam, 2002).

Commercial use of Tl as an alloying element is limited due to its toxic properties. In recent years, its largest use (60–70%) was in the electronic industry. It is added to the production of special refractive glass and several other specific tools. Tl is also used as radioisotopes in medicine for scintigraphy. Its previous use in pesticides (rodenticides and insecticides) has been recently forbidden. Tl and its compounds are extremely toxic, and should be handled with great care.

B SOILS

The Tl contents of soil groups range from 0.014 to 2.8 mg/kg, and average 0.5 mg/kg (Table 18.2). Its higher levels are in Cambisols and Histosols, what reflex its association with both clay fraction

and SOM. Its occurrence in uncontaminated soils from different countries is reported as follows (in mg/kg):

- Canada: garden soils, 0.17–0.22 (Fergusson, 1990)
- China: 0.21–2.4 (Govindaraju^{1313s})
- France: 1.54–55 (Tremel et al.¹⁵²¹)
- Japan: 0.39–0.59 (Takeda et al., 2004)
- Poland: 0.01–0.41 (Łukaszewicz et al., 1996)
- Sweden: <0.04–0.52 (Eriksson, 2001)
- U.S.: 0.02–2.8 (Smith and Carson⁷⁴⁰)

Geochemical behavior of Tl is analogous to that of K. Tl reveals a great affinity to micaceous minerals and inhibits the activation energy of K released from these minerals.⁹⁹⁹ During weathering, Tl is readily mobilized and transported together with alkaline metals. However, Tl is most often fixed by clays and Mn and Fe hydroxides. The sorption of Tl by SOM, especially under reducing conditions, is also known. Tl may be immobilized and oxidized to Tl⁺³ by sulfides in the terrestrial environment (Sager¹⁴⁷⁴). Medved et al. (2008) reported that majority of Tl in soils is associated with the residual fraction, and thus remains immobile and slightly phytoavailable. Its mobility in soils is reported to be due to acid rain. According to Tremel et al.,¹⁵²⁰ elevated Tl levels, up to 40 mg/kg, is observed in soils derived from Tl-rich parent material. Elevated Tl content (average 59 mg/kg) in O horizon of the forest soil in Sweden is presumably affected by strong sorption by OM (Tyler, 2005). The Tl concentration in German soils, at the range of 0.2–4.0 mg/kg, decreased by 10–15% of the HNO₃—extractable fraction at pH < 7.0, within 14 years (Crössmann, 1994).

Anthropogenic sources of Tl in soils are related to coal combustion, metal smelting, refining processes, and cement industry that is considered to be its largest emitter. Flue dust from cement plants contain Tl at the range of 42–2379 mg/kg, with mean value of 428 mg/kg (Scholl, 1980). Schoer¹⁴¹ reported the range of 3–6 mg/kg in soils in the vicinity of a cement plant, and Sager¹⁴⁷⁴ found Tl maximum content in such soils at 15 mg/kg. As reported Xiao et al. (2004a,b), Tl levels in various samples from the vicinity of mining region in China range as follows (in mg/kg): (1) soils, 40–124; (2) wash materials, 20–28; (3) alluvial deposits, 14–62; (4) undisturbed soils, 1.5–6.9; (5) and background soils, <0.2 to 0.5. Asami⁹²⁶ cited that soils around abandoned Hg mines in China contain Tl within the range of 20–80 mg/kg. Soils of an Hg mineralization area in Russia have Tl within the range of 0.03–1.1 (Dvornikov et al.¹⁹⁹). Waste tips from the Zn–Pb mine in Poland contain Tl at mean level of 39 mg/kg (Wierzbicka et al., 2004). Adamiec and Helios-Rybicka (2004), reported the Tl range of 3.1–146 mg/kg in surface soils in surrounding of the Zn–Pb industry in Poland. Elevated Tl levels, from 8.8 to 27.8 mg/kg, are also reported for soils in the vicinity of Pb and Zn mines in Germany.¹⁵²⁰

In general, soil Tl contents above 1 mg/kg indicate pollution and this concentration is proposed as the MAC value for agricultural soils.

C PLANTS

The Tl content of plants seems to be a function of Tl concentrations in soils, as illustrated in [Figure 18.4](#). Reference content of Tl in plants was calculated by Markert^{1399a} as 0.05 mg/kg. According to Nolan et al. (2004) this element in plant tissues is predominantly as cation Tl⁺.

Herbage and woody plants apparently contain higher amounts of Tl than do other plant species. Dvornikov et al.¹⁹⁹ found Tl in herbage to range from 0.02 to 1.0 mg/kg, and Shacklette et al.⁷¹⁰ cited Tl for pine trees to range from 2 to 100 mg/kg (AW), being higher in needles than in stems. Smith and Carson⁷⁴⁰ gave the following Tl levels in plants (in mg/kg): (1) vegetables, 0.02–0.125; (2) clover, 0.008–0.01; and (3) meadow hay, 0.02–0.025 mg/kg. Grass from Zn–Pb industrial area contain Tl within the range of 0.98–3.46 mg/kg (Adamiec and Helios-Rybicka, 2004). Rape seed can

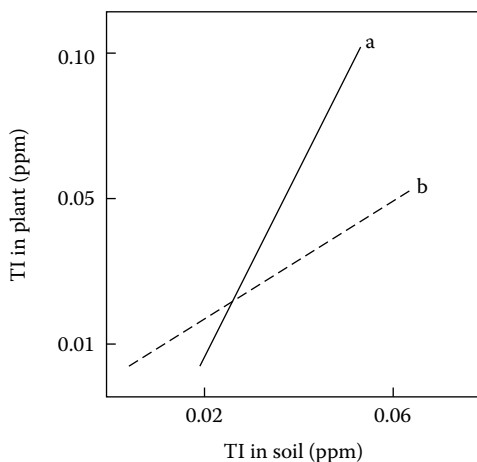


FIGURE 18.4 Tl content of two herbs, (a) wormwood and (b) euphorbia, as a function of its concentrations in soil. (Adapted from Dvornikov, A. G., Ovsyannikova, L. B., and Sidenko, O. G., *Geokhimiya*, 4, 626, 1976 (Ru).)

accumulate large amounts of Tl, up to 33 mg/kg, when grown in soils enriched in this metal.¹⁵²¹ High Tl concentrations, up to 5.5 mg/kg, are sometimes observed in mushrooms.

There is an assumption that some plants, especially of the *Cruciferae* and *Gramineae* families, can serve as hyperaccumulators for phytoremediation of contaminated soils. McGrath¹⁴⁰⁷ reported that there are programs for screening plants (e.g., *Brassica* sp.) for their ability to phytoextract Tl from soils impacted by a cement factory. Zyka⁹⁰⁹ analyzed herbaceous plants grown in soil over Tl mineralization and showed accumulations as high as 17,000 mg/kg (AW) in flowers of *Galium* sp. (*Rubiaceae* family), while other plants accumulated Tl in leaves and stalks at about 100 mg/kg (AW).

Increased Tl levels in plant tissues are highly toxic to both plants and animals. In industrial regions, Tl can be easily absorbed by plants from aerial deposits. Plants grown around coal power plants and cement factories are most likely to have elevated levels of Tl. For example, *Cruciferae* species, near a cement plant in Germany, accumulated Tl up to approximately 450 mg/kg.¹⁴⁰⁷

Anthropogenic Tl in soils seems to be easily mobile and thus readily available to plants. Plants of the *Brassicaceae* family grown in soils contaminated by tailing dam waste accumulated up to 5 mg/kg; the highest EF values were 321 and 607, depending upon the species (Madejon et al., 2007). Several experiments have been conducted on the hyperaccumulator *Iberis intermedia* (Al-Najar et al., 2001; Nolan et al., 2004). This plant may accumulated up to 4000 mg/kg when grown in a soil containing only 16 mg/kg. A higher Tl accumulation in flowers (13.4 mg/kg) than in leaves and stems of *Hirschfeld incana* grown in Tl-affected soils is reported by Madejon et al. (2005).

Al-Najar et al. (2003) observed the high uptake capacity for Tl and the subsequent marked depletion in the rhizosphere soil of two Tl hyperaccumulator plants: kale (*Brassica oleracea acephala*) and candytuft (*Iberis intermedia*). This Tl depletion in the rhizosphere indicates that the transport of Tl to roots is mainly diffusion driven. The data indicate the efficiency of these plants in the Tl phytoextraction.

The Tl concentration in roots up to about 2 mg/kg, can inhibit germination, plant growth, and chlorophyll content. The concentration of 5 mg/kg Tl in the solution decreased, by 50%, the length of roots of collard and wheat, with no visual symptoms of Tl toxicity.¹⁰⁰⁹ Plants especially sensitive to increased levels of Tl are the *Leguminosae* species, cereals, tobacco, and buckwheat. Microorganisms are reported to be relatively sensitive to Tl, and therefore the inhibition of the nitrate formation in Tl-polluted soils may have an agronomic concern. There is also an opinion that Tl is likely to be involved in microbial cycling by possible methylation.⁸⁵⁶

19 Elements of Group 14 (Previously Group IVa)

Trace elements of Group 14 are silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). Geochemical properties and terrestrial abundance of these elements diverge widely. Their common characteristics are the weak solubility of their hydroxides and oxides in water and affinity to bond with oxygen. All elements have variable valences, +2 and +4 (Table 19.1), and only Si is a metalloid (nonmetal). Other elements of this group, Ge, Sn, and Pb, are metals and show chalcophilic properties in the terrestrial environment.

I SILICON

A INTRODUCTION

Silicon, especially in a combination with oxygen, is the basic nonmetallic components of all rocks and is considered as a trace element only in respect to its biochemical function. It is the second most abundant element in the lithosphere and comprises 25.7% (by weight) of the Earth's crust. In the lithosphere it is the most stable element, preferable at +4 oxidation state and occurs mainly as SiO_2 (Table 19.1). However, under specific conditions, it can be dissolved and transported, mainly in colloidal phase.

Quartz, SiO_2 , is a very resistant mineral in all terrestrial compartments and is the basic component of all silicates (e.g., feldspar, quartz) and aluminum silicate minerals. Nonsilicate mineral containing Si is silicon carbide (carborundum), SiC .

Due to versatile properties of Si, it is used in many different sectors of manufacture of some steels, aluminum alloys, glass, and refractory materials. Si is considered a semiconductor and thus it is an important commodity in the computer manufacturing business. Semiconductor-grade silicon is used in the manufacture of silicon chips and solar cells. It is also utilized in the production of ceramics, cements, papers, and textiles, as well as in several other productions, including insecticides, cosmetics, and pharmaceuticals. Si-NP may have an application in the chemotherapy.

B SOILS

Silicon is the most abundant element in soil, averages 54%, but in some soils its content is much higher (Table 19.2). Takeda et al. (2004) presented the data for average SiO_2 contents in different soil groups, as follows (in %): (1) Andosols, 43; (2) Cambisols, 56; (3) Gleysols, 63; and (4) Acrisols, 66.

Quartz, SiO_2 , is the most resistant mineral in soils and is also known to occur in a noncrystalline form, opal, which is presumable of a biological origin. In soils, amorphous silicates apparently contribute to anion adsorption processes, and it has been suggested that silicate and phosphate ions compete for sites on mineral soil particles.⁵³⁰ Tiller⁷⁹³ showed that the presence of monosilicic acid in solution increases the sorption of trace cations, such as Co, Ni, and Zn, by clays.

A part of Si is released from minerals into the soil solution and this process is controlled by both soil and climatic factors. Carlisle et al.¹²¹ reported that soluble Si (mainly as H_4SiO_4) in the soil solution ranges from 1 mg/L to about 200 mg/L. Soil pH has an especially marked effect on Si concentrations in solutions, although the mobility of Si in soils cannot be predicted accurately from

TABLE 19.1
Selected Properties of Trace Elements of Group 14

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C) (g/cm ³)	Valence ^b
Si, silicon	14	28.08	117	2.33	+2, +4 [−4]
Ge, germanium	32	72.61	152	5.23	+2, +4
Sn, tin	50	118.71	172	7.31	+2, +4
Pb, lead	82	207.20	181	11.35	+2, +4

^a Approximate average values for the main oxidation states.

^b Valence value in bold are from the main oxidation states.

the pH alone. Usually, Si is more mobile in alkaline soils, but as Carlisle et al.¹²¹ described, increasing the pH to about 9 decreases the Si concentration in solutions.

Several interferences between Si and other ions such as P, Al, Ca, and Fe may occur in soil and modify the behavior of Si. For example, in acid soils, silicate and phosphate ions form insoluble precipitates that may fix several other cations (e.g., Fe and Al oxides that have a marked capacity to fix dissolved Si as H₄SiO₄). Appreciable amounts of SOM in flooded soil induce a higher Si mobility, apparently due to the reduction of Fe hydrous oxides, which release adsorbed monosilicic acid.

C PLANTS

Silicon in the form of H₄SiO₄ (known as dissolved silicate) is readily absorbed by plants and is often deposited as a solid amorphous Si, opal. It may be taken up in a form of monosilicate acid,

TABLE 19.2
Abundance of Trace Elements of Group 14 in Rocks and Soils (mg/kg)

Rock/Soil	Si (%)	Ge	Sn	Pb
Earth's crust	26–29	1.4–1.6	2.3–2.5	14–15
Igneous rocks				
Mafic	20–30	0.7–1.5	0.3–1.5	0.1–8
Acid	31–34	1.0–1.5	1.3–3.6	10–25
Sedimentary rocks				
Argillaceous	25–28	1.0–2.5	6–10	14–40
Sandstones	30–40	0.8–1.4	0.5–0.7	5–10
Calcareous	5–30	0.1–0.3	0.3–0.5	3–10
Soils ^a	54 ^{bx}	2.0 ^b	2.5 ^b	27 ^b
Arenosols (sandy)	—	0.6–2.1	<0.1–2	5–40
Podzols (medium loamy)	—	1–2.5	0.3–2	10–57
Cambisols (heavy loamy)	—	1–2.5	0.3–4.2	10–90
Calcisols (calcareous)	—	0.5–1.3	<0.1–1.8	17–65
Histosols (organic)	—	0.8–1.6	0.2–7.9	3–84

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil average (Table 3.2).

^{bx} Average estimation for SiO₂.

amorphous silica, and as organic complexes (Körös¹⁰⁵⁵, Richmond and Sussman, 2003). The Si absorption depends on its concentration in solution, soil water regime, and pH.

Silicon is a common mineral constituent of plants; however, it has been not defined to be essential. Its amounts vary greatly, mainly upon plant species. For example, mean Si contents in grasses range between 0.3 and 1.2%, whereas its concentrations in leguminous vary from 0.05% to 0.2%. Some species may accumulate much higher amounts of Si, up to >10%, for example, sedges, nettles, horsetails, and diatoms (Epstein, 1994). Rice plants are also known as accumulators of Si and may contain it up to 10% in hulls and up to 4% in grains (Alyoshin et al.⁹²⁰).

There is an evidence for two mechanisms of Si uptake: passive in grasses and several other plants and active in rice (Tinker⁷⁹⁸). Plants reveal an ability to restrict the uptake of Si, excluding H_4SiO_4 at the external root surface or bind it within root tissues, and thus can reduce the concentration of Si in the xylem sap to about 6% of that in the external solution.¹²¹ Although Si-organic complexes have not yet been isolated, plant Si has been shown to exist in at least two forms, one of which is believed to be a hydrogen-bonded Si-organic complex.¹²¹ Körös¹⁰⁵⁵ reported that a special silicon complex (thujaplicine complex) was isolated from *Thuja plicata* and that the most of Si taken up, either as monomeric silicic acid or as organic complex, was deposited in plant tissues as opal silica. Where large amounts of Si are accumulated, intercellular deposits can be formed as plant opal. Residues of such plants contribute to the formation of amorphous silica in soils.

Silicon has not yet been known as an essential element for higher plants because its role in plant biology is poorly understood (Epstein, 1999). However, recent studies confirmed that Si is an important element that increases the tolerance of plants against environmental stress (Savant et al., 1999). It is also believed that Si is necessary for plant growth, development, and structure strength (Richmond and Sussman, 2003). Si (possibly as amorphous silica) impregnates walls of epidermal and vascular tissues.³⁸⁷ Thus, Si strengthens plant tissues, reduces water loss, and retards fungal infection.

Wallace⁸⁴⁰ reported that soluble Si stimulated plant growth. This stimulation seems to be related to the observed effects of Si on increased P and Mo uptake by plants, as well as on Mn transport within plant tissues.³²⁶ Antagonistic effects of Si on the uptake of B, Mn, and Fe were also observed (Figure 5.8). Si seems to inhibit deleterious effects of As and Ge on mitochondria activities in rice grains,⁹¹⁹ as well as reduce the internal phytotoxicity of Al and Mn (Foy et al.,²⁴¹ Rogall and Römheld, 2002). The ameliorative effect of an increase in readily available H_4SiO_4 on reducing the toxicity of Al and Mn is apparently related to cation/anion balance at the root surface, which leads to the immobilization of these elements. Alyoshin et al.^{919,920} observed a beneficial impact of Si on metabolic processes in chloroplasts and on phosphorylation processes in rice grains.

Miyake and Takahashi⁵⁴⁶ reported that the Si deficiency inhibits the reproductive growth of tomato plants grown in culture solution. The deficiency of phytoavailable Si in soils of rice-growing regions may have deterioration impact on rice crop due to decreased resistance to some diseases, such as blast, brown spot, and stem rot (Rush and Lee, 1992; Roy, 1996). These effects can be minimized by using Si-fertilization (Seebold et al., 2001). Rodrigues et al. (2003) have confirmed positive effects of available Si in the plantations of rice in Brazil. It has also been cited that Si may increase the drought tolerance of plants (Lux et al., 2002). According to Gong et al. (2005), the addition of phytoavailable Si improves drought tolerance of wheat plants, increasing antioxidant defense abilities and other physiological processes (e.g., photosynthesis) under drought conditions.

II GERMANIUM

A INTRODUCTION

The Ge concentration in the Earth's crust averages within the range of 1.4–1.6 mg/kg (Tables 3.2 and 19.2). Its similar contents are found in igneous rocks. Ge concentration in argillaceous sediments ranges from 1 to 2.5 mg/kg, and in calcareous rocks it is below 0.3 mg/kg.

Chemical characteristics of Ge and Si are similar and both occur preferably in the +4 oxidation stage (Table 19.1). Ge exhibits variable properties: lithophilic, siderophilic, and chalcophilic, and may readily substitute Si in silicate minerals. Its common minerals are germanite, $\text{Cu}_3(\text{Ge,Fe})\text{S}_4$ and argyrodite, Ag_8GeS_6 . It is likely to be associated with Pb–Zn–Cu sulfide ores.

Germanium is readily fixed by OM and, apparently, this might explain its elevated contents in several coals. In most coals, Ge concentration ranges from about 1.6 to 13.4 mg/kg (Meij and Winkel, 2004).

Total world Ge production in 2008 was estimated as 105 t (USDI, 2009). Generally, it is a by-product obtained from smelter dusts during the Zn production, from Pb–Zn–Cu sulfide ores as well as from by-products of coal combustion. The Ge emission from coal burning is calculated globally as about 700 t/year. Font et al. (2005) described that Ge species generated during coal gasification may be extracted from fly ash. According to Hernandez-Exposito et al. (2006), Ge recovery from fly ash, by means of ion flotation is highly effective, at 100% of its content.

Germanium is an important commodity in several manufacturing sectors, such as optical fiber and infrared optic systems, polymerization catalysts, electronic and solar electrical applications, and in metallurgy. It is also used in chemotherapy and is used as a strong pain reliever. Its organic compounds are used in the Asian medicine (Moskalyk, 2004).

B SOILS

Data on the Ge abundance in soils are rather scanty. Its contents average 2.0 mg/kg and vary within the range of 0.5–2.5 (Table 19.2). No association with soil groups is observed. Increased Ge levels (up to 95 mg/kg) in soils of Sweden are most probably an effect of contamination (Eriksson, 2001). Its contents in soils, as reported by other authors, are (in mg/kg) (1) United States, 0.1–2.1 (Shacklette and Boerngen⁷⁰⁶; (2) Sweden, 0.05–0.64 (Tyler and Olson, 2002); and (3) reference soils of China, 1.2–3.2 (Govindaraju¹³¹³).

During weathering, Ge is easily mobilized, mainly as $\text{Ge}(\text{OH})_2$, and transported in aquatic systems, but then it is readily fixed, apparently in the form of $\text{Ge}(\text{OH})_4$, by clay minerals, Fe hydroxides, and OM. In soils, Ge occurs mainly as divalent cations, but its complex anions are also known, such as HGeO_2^- , HGeO_3^- , and GeO_3^{2-} .

Kurtz et al. (2002) described the Ge behavior during soil weathering, using the Ge:Si system as a tracer of silicate weathering processes. They indicated that the Ge concentration in soils increases with Si, and decreases with Fe. However, the Ge:Si fractionation is not related to Ge–Fe or Ge-organic associations. Sequential extraction experiments indicated that the most of soil Ge is associated with secondary silicate fractions. Scribner et al. (2006) observed that in soils developed on basaltic lavas (Hawaii), elevated Ge:Si ratios are the effects of the Ge fixation by clay minerals and by some nonsilicates.

C PLANTS

Plants seem to absorb Ge at a relatively high rate, possibly in the form of GeO_2 ; however, it is not known to have any physiological functions. Rice plants may accumulate Ge readily and concentrate this element to a level as high as 1% (AW) in tops, although Ge is highly toxic to plants and to rice plants, in particular.⁵¹⁶ It is assumed that interaction between Ge and Si exists and that those plants that need Si for the growth are most sensitive to Ge. Even at low concentrations, Ge was shown to inhibit germination and plant growth.^{679,919} The radioactive ^{68}Ge was used previously as a Si tracer in biological materials. Nikolic et al. (2007) tested its suitability for the study of Si transport in higher plants and have concluded that ^{68}Ge -traced Si uptake by four crop species is widely different.

Schroeder and Balassa⁶⁹⁵ gave the range of Ge concentrations in grains as 0.09–0.7 mg/kg (FW) and in vegetables as 0.02–1.07 mg/kg (FW). Duke¹⁹⁷ found Ge in food plants of a Central American

region to range from <0.01 to <0.1 mg/kg. Connor and Shacklette¹⁴⁵ reported the Ge content of plant ash, if detected, to an average of 20 mg/kg, but the element was rarely detected. Ge was found in only one of 123 samples of Spanish moss (*Tillandsia usneoides*, *Bromeliaceae* family) at a concentration of 15 mg/kg (AW), and this sample was from an area subject to the air pollution from industrial operations.⁷⁰⁸ The Ge contents of willow leaves grown in the Sudeten Mountains and of Turkish hazel grown in Wrocław city (Poland) varied within the ranges (in mg/kg) 12–108 and 14–100, respectively. Increased concentrations of Ge resulted from its high industrial emissions.^{1335,1477}

III TIN

A INTRODUCTION

The Sn average content of the Earth's crust is estimated as 2.5 mg/kg (Table 3.2). It is slightly elevated in acid igneous rocks (1.3–3.6 mg/kg) and in argillaceous sediments (6–10 mg/kg) (Table 19.2). Sn exhibits two oxidation states, +2 and +4, and reveals metallic and amphoteric properties, respectively. Sn is a component of only a few minerals, of which the most important source of this metal is cassiterite, SnO_2 . In association with other metals it occurs in stannite, $\text{Cu}_2\text{SnFeS}_4$; teallite, Cu_3SnS_4 ; and montesite, PbSn_4S_3 . The Sn ability to form complexes with organic substances may affect its enrichment in bioliths.

The world Sn production was 333 t in 2002 (USDI, 2009). Most of Sn is used as components of protective coatings and as an alloying element. Due to a large temperature difference between melting (232°C) and boiling (2270°C) points, Sn can be used as an alloy without loss through the vaporization. The metal has a large number of organometallic derivatives, which are of importance in various manufacturing sectors. It is also a commodity for solder, glass making, PVC stabilizers, pesticides, and wood preservatives. Sn is a common component of ship paints, which is of an environmental concern (Hoch, 2001). Also, its elevated emission to the atmosphere, mainly from coal combustion, refuse incineration, and Cu/Ni production facilities may be of a local serious problem (Nriagu and Pacyna, 1988).

Environmental properties and behavior of Sn and its inorganic compounds are broadly reviewed by IPCS (2005).

B SOILS

The abundance of Sn in soils averages 2.5 mg/kg and it is distributed rather uniformly in soil groups, within the range of <0.1 –5, being a bit elevated in Cambisols and Histosols (Table 19.2).

The mobility of Sn during weathering is highly pH dependent. Especially, Sn^{2+} , a strong reducing agent, can be present only in acid and reducing environments. Soluble Sn follows the behavior of Fe and Al and remains in the weathered residue along with hydroxides of these metals. Due to an ability of Sn to form complexes with SOM it is generally enriched in surface soil horizons and in Histosols. Inorganic Sn compounds can be methylated by microorganisms in both water and sediments (Falke and Weber, 1994). However, Me–Sn compounds may also be demethylated (Bluden, 1983).

The occurrence of Sn in soil has not received much studies; only Shacklette and Boerngen⁷⁰⁶ presented comprehensive data on Sn in soils: the range of its mean contents is 0.8–1.5 mg/kg, and the highest amounts, up to 2.0 mg/kg, were found in clay and clay loamy soils. Its contents in soils reported by other authors are as follows (in mg/kg): (1) Germany, 1.0–4.0 (Kick et al.³⁹⁰); (2) Japan, 2–3.1 (Takeda et al., 2004); (3) Sweden, 0.4–8.6 (Eriksson, 2001); (4) China, reference soils, 2.5–17.7 (Govindaraju¹³¹³); and (5) United States, 1.0–11.0 (Chapman¹³¹). Although Sn in soils is largely derived from the bedrocks, its increased level due to pollution has been noticed, for example, up to 1000 mg/kg, near smelter areas (Schafer and Fermfert, 1984). The allowable concentration of Sn in soils is established as 50 mg/kg.¹³⁵⁷

Soil contamination with Sn is mainly from landfills (Huang and Matzner, 2004). Sn compounds are fixed by the clay fraction and metal oxides and are relatively easily phytoavailable. Soil parameters, and in particular CEC, pH, salinity, and kind of minerals, are important in controlling the sorption of organic Sn compounds that are of a great environmental concern (Weidenhaupt et al., 1997).

C PLANTS

There is no evidence that Sn is essential to plants and it is considered as toxic to both higher plants and fungi. When it exists in easily available forms in soils, such as cations Sn^{2+} and Sn^{4+} , it is absorbed by roots, where it is likely to be accumulated.⁶⁶²

The common range of Sn in food plants is reported to be between <0.04 and <0.1 mg/kg, and in grass from 0.2 to 1.9 mg/kg.¹³⁵⁷ Gough et al.²⁷⁹ reported the common range of Sn in plants to be 20–30 mg/kg (AW). According to Duke,¹⁹⁷ the range of Sn concentrations in food plants of the Central American forest region is from <0.04 to <0.1 mg/kg. Its contents in wheat grains are given for various countries as follows (in mg/kg): (1) Sweden, 0.01–0.12 (Eriksson, 2001); (2) United States, 5.6–7.9 (Jenkins, 1980); and (3) Worldwide, 5.6–7.9 (Zook et al.⁹⁰⁶).

According to Tyler and Olson (2005), the R:S (root:soil) ratio for Sn is about 0.1. Whereas Kloke et al.¹⁰⁵² reported that the value of this ratio may widely vary within the range of 0.01–0.1. In beech forest growing in podzolized soil in Sweden, ranges of Sn in various species were (in mg/kg) found to be from 0.2 to 0.3 in *Lactarius blennius* to 1.0–1.8 in *Collybia peronata* (Tyler, 2004).

Plants growing in contaminated soils accumulate Sn to high levels, for example, up to 1000 mg/kg in sugar beet (Peska and Kolsky⁶⁰⁸). Jenkins (1980) reported Sn concentrations between 338 and 2165 mg/kg, and Peterson et al.⁶¹⁰ reported Sn concentrations up to 2000 mg/kg in vegetation near Sn smelters. Sn-resistant bacteria may accumulate this metal up to 7700 mg/kg (Maguire et al., 1985).

IV LEAD

A INTRODUCTION

The average Pb content in the Earth's crust is estimated as 15 mg/kg (Table 3.2). Its terrestrial abundance indicates a tendency for a concentration in the acid series of igneous rocks and argillaceous sediments in which the common Pb concentrations range from 10 to 25 and from 14 to 40 mg/kg, respectively. In ultramafic rocks and calcareous sediments, the ranges are 0.1–8 and 3–10 mg/kg, respectively. It occurs in the environment mainly as Pb^{2+} , although its oxidation state +4 is also known (Table 19.1).

In the terrestrial environment, two kinds of Pb are known: primary and secondary. Primary Pb is of a geogenic origin and was incorporated into minerals at the time of their formation, and secondary Pb is of a radiogenic origin from the decay of U and Th. The ratio of Pb isotopes is used for dating the host materials and identification of pollution sources.

Lead has highly chalcophilic properties and thus its primary form in the natural state is galena (PbS). Its common minerals are anglesite, PbSO_4 ; cerussite, PbCO_3 ; minium, Pb_3O_4 ; pyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$; and mimetite, $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$.

The global production of Pb in 2008 was 3.8 Mt (USDI, 2009) and it is obtained mainly from galena deposits. However, in the United States, above 90% of all Pb is produced from secondary sources, that is, Pb scraps from spent lead-acid batteries.

The largest worldwide use of Pb is for lead-acid batteries. In addition, it is used in solders, alloys, cables, chemicals, and for many other purposes. Nowadays, the use of Pb in petrol as an antiknock additive in developed countries has been phased out in order to reduce the atmospheric Pb pollution.

The overall market for tetraethyl and tetramethyl Pb has declined considerably, but still there are some markets for these chemicals in the developing countries.

The global atmospheric emission of Pb at the end of the last century was estimated as 332 kt/year, and in Europe it was estimated as 85 kt/year (Pacyna and Pacyna, 2001). In the 1980s, the emission of Pb was higher from antiknock additives in gasoline than it was from pollution point sources.

B SOILS

The overall mean value of total Pb for different soils is estimated as 27 mg/kg (Table 3.2). Its background average contents given for soils of different countries vary (in mg/kg) from 18 (Sweden) to 27 (China). Its contents in various soils groups vary within the range of 3–90 mg/kg, being the highest in Cambisols and Histosols. Its lowest background contents up to 40 mg/kg, are found in Arenosols. (Table 19.2).

The Pb distribution in mineral soils shows a positive correlation with fine granulometric fraction. Geometric mean background values for Pb in soils of Poland indicate its growing levels with increasing content of clay granulometric fraction; for example (in mg/kg), (1) 12.6 in sandy soils; (2) 16.4 in medium loamy soils; and (3) 20.9 in heavy loamy soils (Table 4.1).

During weathering, Pb sulfides slowly oxidize and have an ability to form carbonates and also to be fixed by clay minerals, hydroxides, and SOM. Some authors have pointed out that the Pb fixation by SOM is more important than the fixation by hydrous oxides (Li and Shuman, 1996). Basta et al. (2005) described that electronic properties of Pb result in a strong affinity for SOM and formation of inner-sphere metal surface complexes. Pb-SOM sorption increases with increasing pH. The geochemical characteristics of Pb^{2+} somewhat resemble the divalent alkaline-earth group of metals; thus, Pb has an ability to replace K, Ba, Sr, and even Ca, both in minerals and in sorption sites.

The Pb distribution within soil profiles is not uniform and reveals a great association with hydroxides, especially of Fe and Mn. Its concentrations in Fe–Mn nodules may be very high, up to 20,000 mg/kg.¹³⁵⁷ It can also be concentrated in calcium carbonate or phosphate particles. At higher pH (>6), Pb is taken up by the feldspar surface apparently through cation exchange processes, although at high pH a discrete phase of hydrocerussite is also observed (Chardon et al., 2008).

Generally, Pb is accumulated near the soil surface, mainly due to its sorption by SOM. Studies conducted by Sipos et al. (2005) suggest that SOM plays a decisive role in the Pb adsorption, but the fixation by clay minerals is much stronger. The mobilization of Pb is usually slow, but some soil parameters, such as increased acidity, formation of Pb–OM complexes may increase its solubility. On the contrary, Steinnes and Friedland (2005) reported that Pb is likely to concentrate in deeper horizons of podzolic forest soils from Norway, whereas this phenomenon was not observed in the United States sites. Barkopuch et al. (2007) described complex physicochemical and hydrodynamic parameters that control the Pb transfer in agricultural soils.

The Pb concentrations in soils solution are relatively low (<1–60 $\mu\text{g/L}$), and highly depending on the methods used for obtaining soils solution. It occurs in the soil solution as cationic species: Pb^{2+} , PbCl^+ , PbOH^+ , and as anionic species: PbCl_3^- and $\text{Pb}(\text{CO}_3)_2^{2-}$ (Kabata-Pendias and Sadurski, 2004). Pb in soil solution may easily move from the upper horizons to lower causing pollution of groundwater (Alumaa et al., 2002). Perelomov and Kandeler (2006) observed that due to microbial activities, Pb concentration increases in soil solutions and decreases at the surface of Fe-minerals. According to Pampura et al. (2007), the predictability of FMI values for Pb in soil solution is high and may be useful for the critical load calculation.

The background Pb content of soil is inherited from parent rocks. However, due to the widespread Pb pollution, most soils are likely to be enriched in this metal, especially in the top horizon. A great deal of data are available in the literature on soil Pb, but sometimes it is difficult to separate the data for background Pb levels in soils from those of anthropogenically influenced amounts in

surface soils. Average Pb contents given for soils of different countries vary within the range of 18–32 mg/kg (Table 3.2). However, Pb-range values given for various soils groups are much higher, up to 90 mg/kg in Cambisols (Table 19.2), which indicates contamination.

Gough et al.¹⁰¹² found a relatively low Pb content of soils in Alaska. Although Pb in these soils ranges from 4 to 349 mg/kg, about 90% of the samples contained only up to 20 mg/kg, with a geometric mean of 12 mg/kg. Lower baseline Pb levels (median 2.6 and 9.5 mg/kg, in sandstone soils and limestone soils, respectively) are reported for soils under semiarid condition of Brazil (Melo et al., 2006). Low concentrations of Pb in soils from this remote region suggest that baseline values of this metal in most world soils should not be much higher than 20 mg/kg. This corresponds closely to the lithogenic concentrations of Pb, which do not exceed the above value, with the exception of argillaceous sediments (Table 19.2).

The Pb levels of soils that are toxic to plants are not easy to evaluate, especially that it is not easy to assess how much of soil Pb is available to plants. Davies¹⁶⁵ stated that an upper limit for the Pb content of an unpolluted soil could be established as 70 mg/kg. Similar value, 60 mg/kg, is established in China for tea garden soils (Jin et al., 2005). The soil Pb concentration of 450 mg/kg in a play area for children is proposed by the SGV10 (DEFRA, 2002). The MTL value for Pb in soils of South Africa is accepted as 56 mg/kg, at its range of 2.99–65.8 mg/kg (Herselman et al., 2005).

1 Reactions with Soil Components

Lead is the least mobile among the other trace metals in soils, although its sorption is reported by Vega et al. (2007) to be lower than that of Zn and Cu. The Pb species can vary considerably from one soil type to another. From results presented by Norrish,⁵⁷⁰ Riffaldi et al.,⁶⁵³ Tidball,⁷⁸⁷ and Schnitzer and Kerndorff⁶⁹⁰ it may be concluded that Pb is associated mainly with clay minerals, Mn oxides, Fe and Al hydroxides, and SOM. However, in some soils, Pb may be highly concentrated in calcium carbonate particles or in Phosphate concentrations. Phosphates added to a soil contaminated with Pb slightly decreases its easily soluble fraction, and to a greater extent, oxide, and carbonate fractions, while increasing organic fractions, and especially, residual fractions (Figure 19.1). In soils heavily polluted with Pb, the formation of pyromorphite, $\text{Pb}_3\text{Cl}(\text{PO}_4)_3$, is observed.¹²⁶³ The concentration of this mineral is mainly close to grass roots (*Agrostis capillaris*) and indicates an influence of the rhizosphere on processes of its formation.

The Pb solubility can be greatly decreased by liming. A high soil pH may precipitate Pb as hydroxides, phosphates, or carbonates, as well as promote the formation of Pb-organic complexes that are rather stable. Increasing acidity may increase the Pb solubility, but this mobilization is

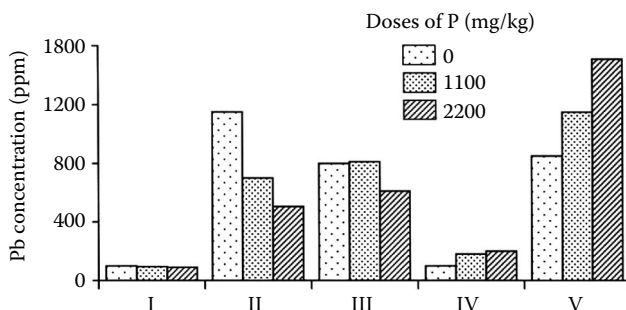


FIGURE 19.1 Phosphate (KH_2PO_4) effects on Pb fractionation in the Pb-contaminated soil (Pb–2800 mg/kg, pH ca. 7.0, after CaCO_3 addition). Fractions of Cd (after Tessier, A., Campbell, P. G. C., and Bisson, M., *Analyt. Chem.*, 51, 844, 1979): I, exchangeable; II, carbonate; III, oxide; IV, organic; and V, residual. (From Hettiarachchi, G. M., et al. *Proc. 4th Intern. Conf. Biogeochem. Trace Elements*, Berkeley, CA, June 23–27, 463, 1997. With permission.)

usually slower than its accumulation in organic-rich layers of soils. According to Jin et al. (2005), SOM is the most important factor increasing the Pb bioavailability. The characteristic localization of Pb at surface layer in most soil profiles is primarily related to the accumulation of SOM. Therefore, SOM should be considered as an important sink of Pb in polluted soils. Logan et al. (1997) reported that HA has a high maximum binding capacity for Pb, which is 0.564 mmol Pb²⁺/g, at pH 5.

Hildebrand and Blume³¹⁹ reported that illites show much greater affinity to sorb Pb than other clay minerals, whereas this reaction was not observed by Kabata-Pendias³⁷⁷ in studies of Pb sorption by clays over a wide range of pH. Farrah and Pickering²²⁸ emphasized that adsorption of Pb is highly dependent on the kinds of ligands involved in the formation of hydroxy complexes of Pb [e.g., PbOH⁺ and Pb₄(OH₄)⁴⁺]. These authors discussed several possible mechanisms of adsorption of hydroxy species and suggested that Pb sorption on montmorillonite can be interpreted as simply cation exchange processes, while on kaolinite and illite Pb is rather competitively adsorbed. Abd-Elfattah and Wada² found a higher selective adsorption of Pb by Fe oxides, halloysite, and imogolite than by humus, kaolinite, and montmorillonite. In other studies, the greatest affinity to fix Pb was reported for Mn oxides.^{377,525}

2 Contamination of Soils

Soil pollution due to Pb from mining and industrial activities is not a new problem. Historical evidence suggests that problem of increased Pb in the environment began when our ancestors learned the use of fire. The old industrial Pb contamination has been reported for several countries.^{1272,1547} As Baron et al. (2006) estimated, using Pb isotopes, between 40% and 100% of the total Pb in contaminated soils in France comes from the Medieval workshops.

The fate of anthropogenic Pb in soils has recently received much attention because this metal is hazardous to man and animals from two sources: the food chain and soil dust inhalation or geophagia (pica for soil).

The steadily increasing amounts of Pb in surface soils, both arable and uncultivated, have been reported for various terrestrial ecosystems. The impact of land use on the Pb levels in topsoils is illustrated by Blum et al.¹²³¹ Variable filtration of the atmospheric deposition by the plant canopy affects the Pb input to topsoils, which is three times higher in spruce forest (90 mg Pb/L) than in pasture soil (30 mg Pb/L). Several reports on elevated Pb concentrations in the vicinities of nonferrous metal processing industries were reported (Table 19.3). The accumulation of Pb in surface soil exposed to various pollution sources at some sites has already reached a value as high as 135,000 mg/kg. In mining areas, Pb may be dispersed due to the erosion and chemical weathering of tailings. The severity of these processes depends on chemical characteristics, and the minerals present in the tailings (da Silva et al., 2004).

Increased Pb levels in topsoils are also resulted from Pb shots in hunting areas (Darling and Thomas, 2003; Wolz et al., 2003). Also, soils of military shooting ranges are reported to be highly contaminated with Pb. Robinson et al. (2008) calculated that over 400 t of Pb enters Swiss soils annually at these military sites. The mean Pb concentration in rhizospheric soils was 10,171 mg/kg, which resulted in elevated Pb levels in some plant species above 30 mg/kg, which is toxic to livestock. Further problems are associated with leaf contamination due to soil dust.

Peat bogs are good records of atmospheric Pb deposition due to their great capacity to accumulate and strongly fixate this metal. The anthropogenic Pb deposition extending back at least to Greek and Roman times has been traced in peat cores of several European countries. The Pb concentrations in recent peat bogs are about 100 times higher than the preanthropogenic pollution.¹⁴⁸⁷ Peat soils are regarded as sink of atmospheric deposited Pb and might be a significant source of this metal to the fluvial system due to peat erosion processes (Rothwell et al., 2008).

Researches on Pb compounds in contaminated soils are reviewed by Hildebrand,³¹⁸ Olson and Skogerboe,⁵⁸² Harmsen,³⁰⁵ Zimdahl and Hassett,⁹⁰³ and Wixson and Davies.¹⁵⁴⁷ The main Pb pollutants emitted from smelters occur in mineral forms (e.g., PbS, PbO, PbSO₄, and PbO • PbSO₄), while

TABLE 19.3
Lead Contamination of Surface Soils (mg/kg)

Site and Pollution Source	Mean or Range of Content	Country	References
Old mining area	51–21,546	Great Britain	165, 166, 808, 659
Nonferrous metal mining	170–4563	Great Britain	165, 166
	>300	Germany	390
	15–13,000	U.S.	330
	21–3044	Russia	567
Metal processing industry	291–12,123	Canada	363
	137–14,000	Belgium	1142
	1250–18,500	Greece	559
	628–1334	Holland	305
	53–2100	Japan	403, 926
	104	Norway	732
	2480; 8000 ^d	Poland	871, 507, 1015, 1357
	3170	Romania	1126
	500–6500	U.S.	538
	3074	Germany	1075
	92–2580	Zambia	573
	1612–3640	Russia	854, 1502a
	36,234	Czech Republic	Komarek et al. (2007)
Battery manufactory site	881–1058	Chile	1139
	93–3800	Poland	945
	135,000	U.S.	1166
Urban garden and urban vicinity	6–888	Canada	585
	270–15,240	Great Britain	48, 785a, 959
	10–897	Jamaica	1347
	165–12,750	Poland	159, 1015a, 1173
	127–388	Germany	1046, 1051
	218–10,900	U.S.	127, 208, 628
Sludged farmland	175–3916	Great Britain	59, 987
	60–253 ^a	Japan	395
	80–254 ^b	Holland	314
	>800 ^c	Germany	1023
Roadside soil	132–397	Japan	395
	167–2115	Poland	1173
	114–885	Germany	397
	960–7000	U.S.	582
Application of waste lime	2400	Poland	1173

^a Paddy soil.

^b 6 and 16 t dry matter sludge/ha/year, for 5 years.

^c Soils with dredged sediments.

^d Maximum values for the industrial Silesia region.

Pb in automobile exhausts is mainly in the form of halide salts (e.g., PbBr, PbBrCl, Pb(OH)Br, and (PbO)₂PbBr₂). Exhausted Pb particles are unstable and readily get converted into oxides, carbonates, and sulfates. Processes of methylation of some species of Pb are either biological or purely chemical reactions. As Beijer and Jernelöv⁹³⁵ stated, the conversion of tetraalkyllead compound in soils is most probably not a biological process.

Other important sources of Pb in soils are Pb-containing paints within the home and garden areas. Thornton¹¹⁶⁴ reported that the geometric mean concentration of Pb in 4650 garden soils of Great Britain is 298 mg/kg. The concentrations of Pb were higher in older homes, which clearly indicates a gradual increase of this metal in garden soils. This phenomenon is closely related to hazardous Pb intake by children as a result of “hand-to-mouth” activity (pica soil). This problem was recently reviewed by Davies (2008) who cited that the US EPA defines a soil Pb hazard as bare soil that contains 400 mg/kg of Pb in a play area or 1200 mg/kg in other parts of gardens. According to McGrath et al. (2004), Pb levels above 1000 mg/kg in contaminated soils create a hazard to cattle farms.

The Pb contamination of roadside soils was, for quite a time, of a real environmental concern. Although Pb additives in petrol are banned in most countries, increased Pb levels in soil along high traffic road (up to 7000 mg/kg) have been still observed.¹³⁵⁷ Preciado et al. (2007) used Pb isotopes to distinguish an older Pb accumulation (low ²⁰⁶Pb/²⁰⁷Pb ratio) in soils along highways from a newer Pb accumulation. Tetraethyl and tetramethyl Pb present in soils along highways are converted into water-soluble Pb compounds; however, recent laboratory tests indicated that these organic Pb compounds do not leach significantly through soil profile (Ou et al., 1995).

Cunningham and Berti¹²⁶⁶ and Padmavathiamma and Li (2007) reviewed technical and economic issues related to the remediation of metal-contaminated soils. Because Pb is very strongly bound in almost all types of soil, its phytoextraction is rather limited. When Pb is taken up by plants, its translocation to above-ground parts is very poor. The major proportion of Pb is concentrated in root tissues. However, it is promising that dense vegetative cover will stabilize Pb, for a given period, within the rooting zone.

Because Pb enters soils in various and complex compounds, its reactions may differ widely among areas. Indeed, the opinion appears to differ as to whether Pb as a pollutant is a mobile or a stable soil component. Tyler⁸¹⁶ reported that Pb is the most stable metal in forest soil, and the time necessary for a 10% decrease of its total concentration by leaching was calculated to be 200 years for the polluted soil and 90 years for the “control” one. Kitagishi and Yamane³⁹⁵ calculated the period in which the amount of Pb in soil will decrease by one half, to range from 740 to 5900 years, depending on the kind of soil, the water management, and the SOM content. Stevenson and Welch⁷⁵⁹ observed that Pb moved from the topsoil treated with Pb acetate into the subsoil, even though the soil (silty clay loam) was shown to have a high capacity for binding Pb in nonexchangeable forms. This mobility was attributed to the metal leaching as soluble chelated complexes with OM.

In general, several observations of Pb balance in various ecosystems show that the input of this metal greatly exceeds its output (Table 3.13). For example, Hansen and Tjell³⁰⁴ estimated that an annual increase of Pb in Danish agricultural soils is 3.7% of its total amount in the soil. Kjølhold (1997) calculated that Pb loads from various sources applied on Danish agricultural soils vary from <3 to 96 g/ha/year, for lime and sewage sludge, respectively. Agricultural input of Pb varies and according to Eckel et al. (2005) range from 1.3 to 139 g/ha/year, in Norway and France, respectively.

It must be emphasized, however, that contamination of soils with Pb is very irreversible and, therefore a cumulative process in surface soils will continue, even if its inputs are low.

Previously, there was little concern about Pb contamination of soils because of a relative insolubility of adsorbed and precipitated ions of Pb in soils. The strong Pb adsorption in soils may mean that Pb additions to soil are permanent and irreversible. However, the Pb content of roots is correlated to the Pb content of soil, which indicates its uptake by plants. Certain soil and plant factors (e.g., low pH, low P content of soil, organic ligands) are known to promote both Pb uptake by roots and Pb translocation to plant tops.

The accumulation of Pb in surface soils is of great ecological significance because this metal is known to greatly affect the biological activity of soils. This topic has been reviewed by Tyler^{812,813} Andersson,¹⁹ Doelman and Haanstra,¹⁸⁵ and Hughes et al.,³³¹ who showed that increased levels of Pb

in soil are likely to limit enzymatic activity of microbiota and, as a consequence, markedly increase the accumulation of incompletely decomposed soil organic matter, particularly those materials that do not decompose readily, such as cellulose. A significant accumulation of nitrates in soils enriched in Pb was observed by Woytowicz.⁸⁸⁹ The inhibition of microbial processes due to a high Pb level should be expected principally in soils with a low CEC value (Table 4.8). However, in the long run, it may also occur in other soils with a higher CEC.

Niyazova and Letunova⁵⁶⁷ reported a strong tendency of soil microflora to accumulate Pb at a very high rate that was proportional to the metal content of soils (Figure 19.2). Consumers such as earthworms also concentrate Pb from the soil substrata (Table 4.12), which greatly contributes to a secondary deposition of Pb in surface soils. Ma et al.¹⁰⁸⁰ demonstrated a great influence of pH and the SOM content on the worm uptake of Pb, which is significantly stronger in soils with a low pH and SOM than in soils with higher values of these parameters.

Although Pb is a slightly phytoavailable metal and thus difficult to phytoextract, there are several plants (e.g., *Thlaspi* sp., corn, sunflower) that accumulate larger amounts of Pb, especially in roots. Increasing mobility of Pb using chelates or other technologies (e.g., electroosmosis) can stimulate its phytoavailability.¹³³⁸ Honda et al. (2007) reported that common buckwheat is a Pb hyperaccumulator with a high ability for phytostabilization. Greger¹³¹⁶ cited that *Minuartia verna* may concentrate in leaves >1000 mg Pb/kg. Increasing Pb mobility by using various chelators, such as EDTA and DTPA, can stimulate its phytoavailability, and thus the phytoremediation (Jarvis and Leung, 2002; Lim et al., 2004; Chandra Sekhar et al., 2005). The laboratory test conducted by Chandra Sekhar (2005) in the presence of other metals (Ni, Zn, Cr, and Cd) indicated that Pb uptake by *Hemidesmus indicus* decreased by 50% in the presence of Ni, but there were only marginal effects at the presence of Zn, Cr, and Cd. HA increases Pb availability and thus enhanced its uptake by plants (Angin et al., 2008). Besides chelating agents, some other treatments may increase a pool of soluble (available) trace metals in soils based on the use of (1) mineral acids at various concentration; (2) buffered salts, for example, NH_4OAc ; and (3) neutral salts, such as CaCl_2 , MgCl_2 , $\text{Sr}(\text{NO}_3)_2$, and NH_4NO_3 (Houba et al.¹³³⁵).

In situ stabilization of soil Pb was recently investigated. The addition of Fe-rich lime stabilized biosolids and addition of CaCO_3 increased soil pH to 7, that decreased the Pb uptake by tall fescue, *Festuca aurundinacea* (Adriano, 2004). Klitzke et al. (2008) observed that the impact of $\text{Ca}(\text{OH})_2$ on the Pb mobility in soils is complex and may also increase colloidal Pb mobilization in soils.

According to Hettiarachchi et al. (2001), P compounds are very effective in reducing the Pb bioavailability, and P rocks were more effective than P fertilizers. Hashimoto and Sato (2007) studied the Pb-sorption capacity of various waste products and found out that the most effective are poorly crystalline hydroxyapatites. The immobilization of Pb in soils is highly controlled by P and some minerals, especially pyromorphite-type minerals (Kumpiene et al., 2008). Courtin-Nomade

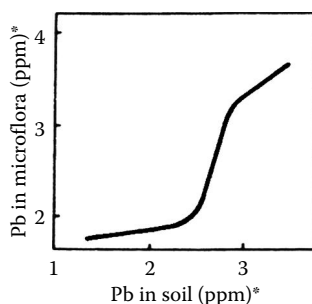


FIGURE 19.2 Concentration of Pb in soil microflora as a function of its content in soil. *Values are given in powers of 10. (From Niyazova, G. A. and Letunova, S. V., *Ekologiya*, 5, 89, 1981 (Ru). With permission.)

et al. (2008) reported that barite (BaSO_4) reveals a susceptibility to incorporate Pb more than other sulfide minerals, what may be of an importance in waste rock pile materials.

Lepp and Dickinson (2003) studied trace metals in an urban woodland ecosystem, where the Pb concentration in soils varied between 347.5 and 76,410 mg/kg, in St. Helens, Merseyside, United Kingdom. They believed that the closed and stable natural vegetation cover, in the absence of human intervention, may be responsible for the bioremediation of polluted soils in St. Helens region.

C PLANTS

Although Pb occurs naturally in all plants, it has not been shown to play any essential roles in their metabolism. Broyer et al.¹⁰⁸ reviewed this topic and concluded that if Pb is necessary for plants, its concentration at the level of 2–6 $\mu\text{g/kg}$ should be sufficient. Pb has recently received much attention as a major metallic pollutant of the environment and as an element toxic to plants.

1 Absorption and Transport

It is not known how much of the soil-Pb might be available to plant. Davies (1995) reported that only about 0.005–0.13% of Pb in the soil solution is available to plants. Wilson and Cline⁸⁸² studied the absorption of ^{210}Pb by barley, using a modified Neubauer technique, and showed that only 0.003–0.005% of the total Pb in soils may be taken up by plants. The Pb uptake, however, varies significantly over the concentration ranges and with various Pb forms that occur in soils. Thus, all plants absorb Pb from soils and transport to above-ground parts (Cannon¹¹⁸). Zimdahl and Koepp⁹⁰⁴ cited an alternate hypothesis to explain the Pb uptake from soil, in which Pb is not taken up directly from soil by plant roots, but rather is sorbed from dead plant materials accumulated near the soil surface. Nevertheless, there is much evidence that Pb is taken up from soils by roots, at both low and high Pb concentrations, and that this process is strongly governed by soil and plant factors.

The Pb uptake by plants depends on several soils properties, such as SOM, granulometric composition, CEC, pH, as well as genetic plant factors, root surface area, and root exudates (Sillanpää and Jansson,¹⁴⁹¹ Davies, 1995). Zimdahl⁹⁰² and Hughes et al.³³¹ extensively reviewed the findings on the Pb absorption by roots and concluded that the mode of its uptake is passive and that the rate of uptake is reduced by liming and by low temperature. The CF values for Pb in the leaves of oleander and lantana is very low, within the range of 0.004–0.038 and clearly indicate that it is neither readily soluble nor easily phytoavailable (Rossini Oliva and Fernandez Espinosa, 2007). Pb is absorbed mainly by root hairs and is stored to a considerable degree in cell walls. The Pb content of plants grown in mineralized areas is, in general, highly correlated with the Pb concentration in soil, although this relationship differs among organs of the plant (Figure 19.3). Nevertheless, Warren⁸⁴⁹ and Kovalevskiy⁴¹⁷ described Pb as a very useful element for geochemical prospecting.

When Pb is present in soluble forms in nutrient solutions, plant roots are able to take up great amounts of this metal, the rate increases with increasing its concentration in the solutions and with time (Figures 19.4 and 19.5). The Pb translocation from roots to tops is greatly limited, and as Zimdahl⁹⁰² described, only 3% of the Pb in roots is translocated to shoots. The significant accumulation of Pb in roots and a low rate of its transport to the other parts of plants are illustrated in Figure 19.6. Meyers et al. (2008) observed that root tissues' uptake of Pb is mainly intracellular and the metal may be aggregated in vacuoles. The main process responsible for Pb accumulation in root tissue is its deposition, especially as Pb-pyrophosphate, along the cell walls. Malone et al.⁵⁰⁶ identified the Pb deposits in cell walls outside the plasmalemma as Pb precipitates and Pb crystals. Similar Pb deposits observed in roots, stems, and leaves suggest that Pb is transported and deposited in a similar manner in all tissues of a plant.

Airborne Pb, a major source of Pb pollution, is also readily taken up by plants through foliage. Much controversy exists in the literature on the question of how much airborne Pb is fixed to hairy or waxy cuticles of leaves and how much Pb is actually taken into foliar cells. A number of studies

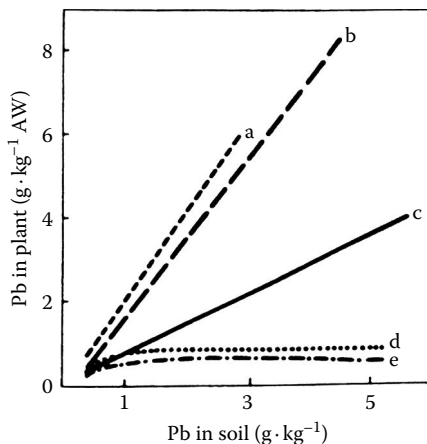


FIGURE 19.3 Concentration of Pb in various organs of larch (*Larix dahurica*) as a function of its content in soil overlying an ore deposit. (a) Roots; (b) bark; (c) needles; (d) twigs; and (e) wood. (From Kovalevskiy, A. L., *Biogeochemical Exploration for Mineral Deposits*, published for the USDI and the NSF, Amerind Publ. Co. Pvt. Ltd., New Delhi, 136, 1979. With permission.)

have shown that Pb deposited on the leaf surface is absorbed by these cells. Although it was suggested that most of the Pb pollution can be removed from the leaf surfaces by washing with detergents, there is likely to be a significant translocation of Pb into plant tissues.³⁴⁰ It has been calculated that up to 95% of the total Pb content of plants may be from aerial deposition on leafy plants.¹²⁷⁰ The significant impact of the aerial Pb source on its levels in mosses (*Hylocomium splendens*) is presented in studies conducted by Migaszewski et al. (2009) who compared the Pb ranges in mosses from the National Park in Poland (7.9–13.6 mg/kg) with its contents in mosses from Alaska (<0.4–1.3 mg/kg).

The phytoavailability of organolead compounds (mainly alkylated Pb) and their toxic effects on plants have recently received much attention. Röderer¹¹³² discussed numerous questions concerning effects of continuous exposure to low levels of organic Pb on plants. Diehl et al.⁹⁷⁹ found that Pb-tetraalkyls in soils are quickly converted to water-soluble Pb compounds that are easily available to plants. Consequently, the vegetation grown in soils polluted with Pb-tetraalkyls show a relatively

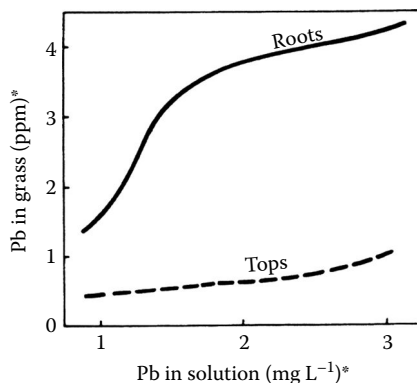


FIGURE 19.4 Pb content of a grass (*Bromus unioloides*) as a function of its concentration in nutrient solution. Note: *Values are given in powers of 10. (Adapted from Kabata-Pendias, A. and Wiacek, K., *Soil Sci. Ann.*, 36/4, 33, 1985.)

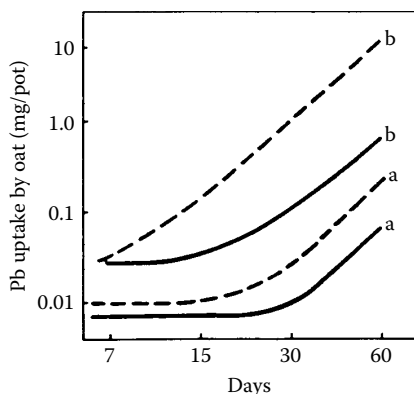


FIGURE 19.5 Pb uptake by oats from sand culture as a function of time and of Pb concentration in nutrient solution. (a) 25 mg/L and (b) 200 mg/L. Solid lines, tops; broken lines, roots. (Adapted from Skripnichenko, J. J. and Zolotaryeva, B. N., *Agrokimiya*, 9, 110, 1980 (Ru).)

large Pb enrichment in both vegetative and generative organs. Zimdahl and Koeppe⁹⁰⁴ summarized results of researches on Pb translocation and uptake and showed that, under certain conditions, it is mobile within the plant. It is generally agreed, however, that Pb from a soil source is not readily translocated to edible portions of plants.

Liu et al. (2003) studied the uptake of Pb by paddy rice and its effect on different rice cultivars. The results of the pot experiment show a great variation in its distribution among different parts of plant, as follows (mean value, mg/kg): (1) roots; 4300 (2) stem, 358.6 (3) leaves, 71.8 and (4) panicle, 16.4. According to these authors, the soil Pb level at 1000 mg/kg affected the growth of rice plant significantly and reduced the crop yield by 11.5%. However, great differences in the tolerance to high Pb concentration are observed, for example, the hybrid rice cultivar (*Shan you 63*) was not affected by 2500 mg Pb/kg in soil (Xie and Huang, 1994).

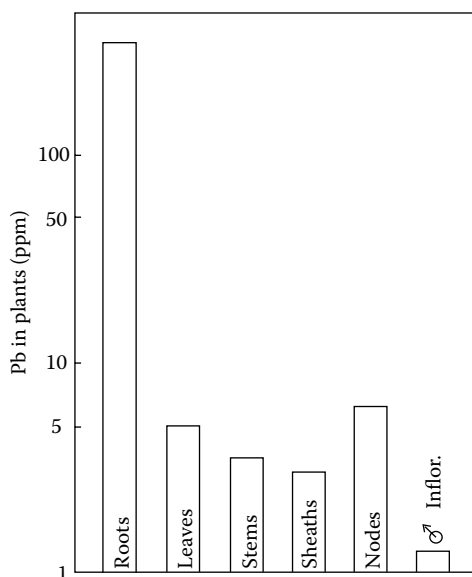


FIGURE 19.6 Distribution of Pb in corn plants grown in the soil with 300 mg/kg Pb. (Adapted from Kabata-Pendias, A. and Wiacek, K., *Soil Sci. Ann.*, 36/4, 33, 1985.)

2 Biochemical Functions

Although there is no evidence that Pb is essential for any plant species, there are many reports on the stimulating effects on plant growth of some Pb salts mainly $\text{Pb}(\text{NO}_3)_2$ at low concentrations. However, the authors often have not considered the effects of anions. Moreover, other reports have described the inhibitory effects of low Pb levels on plant metabolism. Owing to the interactions of Pb with other elements and with many environmental factors, it has not been simple to establish Pb concentrations that are toxic to vital plant processes. Several reports describe toxic effects of Pb on processes such as photosynthesis, mitosis, and water absorption; however, the toxic symptoms in plants are not very specific (Table 5.8).

Subcellular effects of Pb on plant tissues are related to the inhibition of respiration and photosynthesis due to the disturbance of the electron transfer reaction. These reactions are inhibited by Pb concentrations as low as 1 mg/kg in corn mitochondria.⁹⁰² Photosynthesis processes in sunflower leaves were also reduced by half at a Pb concentration of about 1 $\mu\text{M/g}$.¹⁶⁶¹ Pb is likely to be accumulated in various parts of cells, thus affecting their structures. The most deteriorating is the destruction of the plasmalemma, which, in effect, disturbs the permeability for water and leads to impaired plant growth.¹⁵⁵¹ The Pb association with endoplasmic reticulum, as well as with other metal-complexing species may affect its relatively low toxicity (Wierzbicka et al., 2007).

Several plant species, ecotypes, and bacterial strains are able to develop Pb-tolerance mechanisms. This tolerance seems to be associated with the properties of membranes. Lane et al.⁴⁶⁰ stated that Pb becomes strongly bound to cell walls and that pectic acid is most active in the Pb sorption. Thus, Pb has a marked influence on the elasticity and plasticity of cell wall, resulting in an increase in tissue wall rigidity. In the Pb-tolerant plant, *Sesbania drummondii*, a metallothionein gene is involved in the detoxification and homeostasis (Srivastava et al., 2007). In *Arabidopsis thaliana*, the galacturonic acid reveals affinity to fix Pb (Polec-Pawlak et al., 2007).

Sensitive plant species or bacterial strains attract more Pb to their cell walls than do Pb-tolerant plants. A large deposition of Pb on membranes apparently impairs their functions. On the other hand, Pb-tolerant ecotypes may accumulate Pb in inactive forms such as Pb pyro-orthophosphates that have been identified in roots of plants growing under Pb stress.⁹⁰² The behavioral differences between Pb-sensitive and Pb-tolerant bacteria strains are manifested mainly by their growth rates, as is demonstrated with bacterial cultures (Figure 19.7).

Although even a very low Pb concentration may inhibit some vital plant processes, Pb poisoning has seldom been observed in plants growing under field conditions. Zimdahl⁹⁰² discussed this problem and suggested two possible explanations: (1) relatively low Pb concentration in soil and (2) low Pb availability even under contaminated soil conditions.

There are several observations of a high toxicity of organolead compounds to a variety of plants. Toxic effects are related mainly to disturbance of fundamental biological processes such as

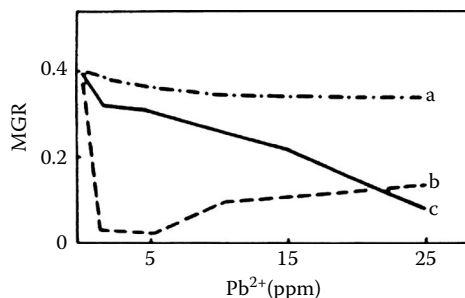


FIGURE 19.7 Influence of PbCl_2 in culture solution on the maximal specific growth rate (MGR) of (a) Pb-tolerant bacteria strain; (b, c) Pb-sensitive bacteria strains. (Adapted from Doelman, P., *Environmental Biogeochemistry and Geomicrobiology*, Ann Arbor Science, Ann Arbor, MI, 989, 1978.)

photosynthesis, growth, mitosis, and so on. As Röderer¹¹³² reported, the toxicity of organic Pb not only exceeds by far the toxicity of its inorganic forms, but the effects caused by both types of agents also differ in quality. This difference is presumably due to various physical and chemical properties of organic and inorganic Pb compounds.

3 Interactions with Other Elements

The interference of Pb with trace elements has been reported only for Zn and Cd (Figure 5.8). The stimulating effect of Pb on Cd uptake by plant roots may be a secondary effect of the disturbance of the transmembrane transport of ions. The Zn–Pb antagonism adversely affects the translocation of each element from roots to tops.

The interference of Pb with Ca is of metabolic importance since Pb can mimic the physiological behavior of Ca and thus can inhibit some enzymes. The beneficial effect of liming on reducing Pb absorption by roots is governed by soil type. In soils where Pb-organic complexes are formed, Ca^{2+} cations do not significantly limit the Pb availability.

A favorable P regime in growth media is known to reduce the effects of Pb toxicity. This interference is due to the ability of Pb to form insoluble phosphates in plant tissues, as well as in soils. S is known to inhibit the transport of Pb from roots to shoots. Jones et al.³⁷⁰ concluded that S-deficiency increases markedly the Pb movement into the tops.

4 Concentrations in Plants

Lead is a major chemical pollutant of the environment, thus, its concentration in vegetation in several countries has increased in recent decades due to anthropogenic activities. This fact has been clearly demonstrated by Rühling and Tyler,⁶⁶⁸ who have reported a several-fold increase of Pb concentrations in the moss *Hypnum cupressiforme* during about a hundred year period, from 1860 to 1970. For this reason, it is important, as Cannon¹¹⁸ stated, that information on the Pb content of plants be documented as to both date of collection and location of the samples. There is a need to collect and preserve samples and data from unpolluted areas throughout the world.

The great variation of Pb contents of plants is influenced by several environmental factors, such as the presence of geochemical anomalies, pollution, seasonal variation, and genotype ability to its accumulation. Genotype factors are observed in distinctive differences. In general, root vegetables are moderate accumulators and leafy vegetables are high accumulators (Alexander et al., 2006). Nevertheless, the Pb contents in plants grown in uncontaminated and unmineralized areas appear to be quite constant, with the range of mean contents for vegetable being 1.5–2.4 mg/kg (being the highest for lettuce) and for cereal grains 0.2–0.5 (Table 19.4). Extremely low Pb levels are reported for wheat and barley grains from Sweden (Eriksson, 2001) and are not included to the calculation of the mean value.

Sillanpää and Jansson¹⁴⁹¹ summarized the results of the worldwide experiment carried out in 30 countries with young wheat ($N = 1723$) and young corn plants ($N = 1892$) and showed that plant-Pb is a function of soil-Pb extracted with AAAC-EDTA solution. Among six soil factors, only soil pH reveals a slight effect on the Pb availability. The frequency distribution of Pb contents of both plants indicated that the most common concentrations range from 0.2 to <1 mg/kg. The highest Pb contents (>1 mg/kg) were observed in plants from Belgium, Hungary, Italy, Malta, and Mexico. European studies carried out under the FAO programs have also indicated a regional variation in Pb contents of young wheat plants (Figure 5.3).

The atmospheric deposition of Pb is apparently a significant source of this metal in above-ground plant parts, as indicated by Dalenberg and van Driel,¹²⁷⁰ by means of ^{210}Pb . Increased Pb levels, up to 165 mg/kg, in edible mushrooms (*Boletus* sp.) grown in a smelting area, also originated from the atmospheric deposition (Komarek et al., 2007).

Increased levels of Pb in both grain and straw of barley grown in the soil heavily polluted with Pb, despite a high soil pH (7.2–7.8) and increased content of carbonates, are often noted. This

TABLE 19.4
Lead in Food Plants from Various Countries^a (mg/kg)

Plant	Range	Mean
Wheat, grains	0.2–0.6	0.5
Wheat, grains ^b	0.005–0.011	0.007
Barley, grains	0.1–0.4	0.2
Barley, grains ^b	0.007–0.028	0.013
Rye, grains	0.06–1.3	0.34
Oats, grains	0.05–2.0	0.34
Bean, pods	1.5–2	—
Cabbage, leaves	1.7–2.4	—
Lettuce, leaves	0.7–3.6	2.4
Carrot, roots	0.5–3	1.7
Onion, bulbs	1.1–2	1.5
Potato, tubers	0.5–3	—
Tomato, fruits	1–3	1.7
Apple, fruits	0.05–0.2	—

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b After Eriksson (2001).

indicated that this soil parameter does not always inhibit the Pb uptake by plants (Figure 19.8). Apparently, this phenomenon is related to disturbed function of biological barriers affected by chemical stress to plants.

There is still a great attention oriented toward the Pb levels in plant foodstuffs, especially bread and potatoes, as a significant source of this metal in human diets,¹²⁴⁷ although recent data reveal a trend toward a global decrease in the Pb emission, mainly because of Pb-free petrol (and probably also due to more precise analytical methods).

The proposed levels for Pb in foods given by the ATSDR (2007) are (in mg/kg, FW), 0.2 and 0.1, for cereals and potatoes, respectively. The average contents of Pb in the main crop plants (wheat and potatoes) from some countries, analyzed during the 1990s, were as follows (in mg/kg, FW): (1) Germany,¹²⁴⁷ 0.02 and 0.06 (2) Poland,¹⁴¹⁶ 0.06 and 0.07, and (3) United States,¹⁵⁴⁹ 0.037 and 0.009.

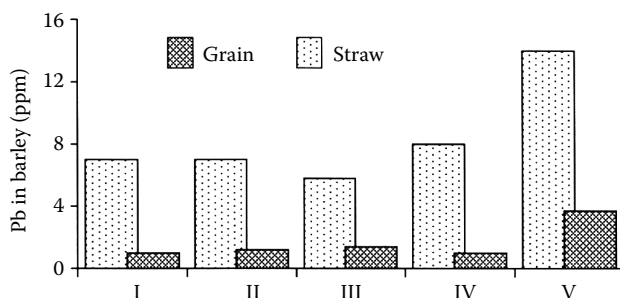


FIGURE 19.8 Impact of Pb added, as Zn and Pb smelter flue-dust, to the soil on the concentration of Pb in spring barley grain and straw. Pb levels in soils (mg/kg) I, 20 (blank); II, 120; III, 320; IV, 1620; and V, 6020. (Adapted from Kabata-Pendias, A. and Pendias, H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 1999, 400 (Po).)

TABLE 19.5

Mean Levels and Ranges of Lead in Grasses and Legumes at Immature Growth from Different Countries (mg/kg)

Country	Grasses		Clovers		References
	Range	Mean	Range	Mean	
Canada	<1.2–3.6	1.8	—	—	237
Great Britain	1–9	2.1	1–3	1.3	369a, 874
Germany	2.4–7.8	3.3	3.3–4.7	4.2	576, 577
Finland	0.19–0.88	0.36	—	—	590
Poland	0.01–35	0.89	1.2–18.8	3.6	1045, 1514
Sweden	5–6	—	—	8.0	668
U.S.	<0.8–5.6	1.6	< 2–15 ^a	2.0 ^a	118, 710
Russia	0.3–10.8	4.6	—	—	1131

^a Alfalfa, calculated from AW basis.

TABLE 19.6

Excessive Levels of Lead in Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Parts	Mean or Range of Content	Country	References
Mining, or mineralized area	Grass, tops	63–232	Great Britain	165, 658, 659
	Maple, stems	135 ^a	U.S.	330
	Birch, twigs	277–570	Russia	417
Metal-processing industry	Blueberry, tops	150	Canada	715
	Blueberry, tops	32–294	Poland	1050
	Lettuce, leaves	596–1506 ^b	Canada	658, 659
	Potato, tubers	350–425 ^a	Canada	848
	Grass, shoots	229–2714	Canada	410
	Chinese cabbage	45	Japan	403
	Lettuce, leaves	45–69	Poland	224
	Carrot, roots	27–57	Poland	224
	Sugar beet, leaves	33–165	Poland	1161
	Blueberry, leaves	141–874	U.S.	357
	Spinach, leaves	322	Zambia	573
Battery manufacturer	Mushroom	<0.5–300	Finland	1069
	Tree foliage	34–459	Canada	480
	Grass, shoots	907–955	Chile	1139
Urban garden and urban vicinity	Spinach, leaves	66	Zambia	573
	Potato, tubers	100–200 ^a	Canada	848
Roadside	Corn, leaves	56	Poland	157
	Corn, leaves	16–24 ^b	U.S.	594
	Grass, shoots	111–186	Germany	397
	Grass, young shoots	67–950	Sweden	669

^a AW basis.

^b Washed and unwashed, respectively.

The Pb background levels of forage plants average (in mg/kg) 2.1 and 2.5 for grasses clovers, respectively, when two extreme values (0.36 in grass of Finland, and 8.0 in clover of Sweden) are excluded from the calculation (Table 19.5). The commonly observed increase in Pb levels in forage plants during the fall and winter seasons is not yet completely understood.

Of great environmental significance is the ability of plants to absorb Pb from two sources, soil and air, even though Pb is believed to be the metal of the least bioavailability and the most highly accumulated in root tissues. The Pb isotopes (206 and 207) concentration of Scots pine (*Pinus sylvestris*) indicates a long time period exposure to atmospheric pollution (Patrick and Farmer, 2007). Several plant species and genotypes are adapted to grow in media with high Pb concentrations; this is reflected by anomalous amounts of this metal in plants when grown in contaminated sites (Table 19.6). The highest bioaccumulation of Pb in general is reported for leafy vegetables (mainly lettuce) grown in the surroundings of nonferrous metal smelters where plants are exposed to Pb sources of both soil and air. In these locations, highly contaminated lettuce may contain as much as 0.15% Pb.⁶⁵⁸

A relatively minor effect of the Pb concentrations in plants has been reported for a contamination of soil due to agricultural activities. Chen et al. (2008) reported that although upward shifting of Pb contents of the vegetable-production soils of California is noticed, no relation to P fertilizer application is observed. The utilization of Pb-enriched sludge has not been practiced for a long period of time; therefore, it is too early to assess the general environmental impact of built-up Pb levels in soils due to repeated sludge use.

20 Elements of Group 15 (Previously Group Va)

Trace elements of the Group 15 are arsenic (As), antimony (Sb), and bismuth (Bi). These elements have similar structure and some similar properties. However, their geochemical characteristics are widely diverging. The variations in electrical charges and in valence states are especially common features of these elements (Table 20.1). The metalloids As and Sb, and the metal Bi are highly chalcophilic. Often As follows P in biogeochemical behavior, especially in aerated systems.

I ARSENIC

A INTRODUCTION

The average content of As in the Earth's crust is estimated as 1.8 mg/kg (Table 3.2). It is found abundantly in argillaceous sediments (up to 13 mg/kg) than in any other rocks (Table 20.2). Its oxidation states are variable, of which As^0 and As^{3+} are characteristic of reducing environments. According to Welch and Lico (1998), As^{5+} is adsorbed preferably by sediments than other As ions.

There are many As minerals, of which about 60% are arsenates. As is highly associated with deposits of several metals and metalloids and therefore is known as a good indicator in geochemical prospecting surveys. Numerous oxide minerals of As are a result of the oxidation of sulfide deposits. These are arsenates and arsenites in which As is combined with some metal (e.g., Fe, Pb, and Cu). The most common As mineral, however, is a sulfide–arsenopyrite (FeAsS). As-rich pyrite is common in the sedimentary formations rich in OM, especially shale, coal, and peat deposits. Its other common minerals are orpiment As_2S_3 ; realgar, AsS ; arenolite, As_2O_3 ; domeykite, Cu_3As ; nikieline, NiAs ; and sperrylite PtAs_2 .

Global production of As was estimated as 53.5 kt in 2008 (USDI, 2009). As is generally recovered from sludge and flue dust during smelting of Cu, Zn, Pb, Au, and Ag ores.

Until the 1970s, about 80% of As was used in the manufacturing of pesticides. Due to its toxicity, the use of As in pesticides has decreased to about 50%, but organic As compounds still dominate the pesticides production (Matschullat, 2000). The rest of As amount is used in wood preservation, photoelectric devices, glassware, and Pb-acid batteries. It is also used to improve corrosion resistance and tensile strength of Cu alloys.

The As content of coal shows extreme variability (within the common range of 0.5–80 mg/kg) and averages 60 mg/kg in fly ash; its elevated level is of an environmental concern. Buat-Menard⁹⁵⁷ calculated the As emission in the northern Hemisphere as follows (in t/year): (1) natural sources (including volcanoes), 4000; (2) anthropogenic sources (industrial and agricultural), 21,600; (3) from terrestrial environments, 20,000; and (4) from aquatic environments, 2000. The total anthropogenic As emission in the 15 EU countries was estimated in 2000 as 176.6 t, and in 2005 as 83.1 t (Pacyna *vide* Zevenhoven et al., 2007). Chilvers and Peterson⁹⁶⁶ calculated that at least 60% of the atmospheric global inputs of As are derived from natural sources, even when a low rate of volatilization of the soil As (0.126% per year) is present.

In several cultures, As compounds have been used for treating human health and it is still used in the traditional Chinese medicine. Using As in medicine and for animal nutrition (still accepted in some countries) should be of concern (Cullen, 2008).

TABLE 20.1
Selected Properties of Trace Elements of Group 15

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C), (g/cm ³)	Valence ^b
As, arsenic	33	74.92	139	5.78	−3, 0, + 3 , +5
Sb, antimony	51	121.76	153	6.69	−3, + 3 , +5
Bi, bismuth	83	208.98	170	9.75	+ 3 , +5

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation states.

B SOILS

The overall mean value of the total As for different soil is estimated as 6.83 mg/kg (Table 3.2). The background contents of various soil groups range from <0.1 to 67, being the highest in Histosols (Table 20.2). The grand mean of soil As is calculated to be the lowest, 4.4 mg/kg, in Podzols, and the highest, 9.3 mg/kg, in Histosols.

The background As levels in topsoils are generally low, although they exceed those in rocks several times. The range in As in soils of the United States is broad, from <0.1 to 93 mg/kg, and the geometric mean for As in surficial materials of the United States is reported to be 5.8 mg/kg.⁷⁰⁷ Similar As content, 9.7 mg/kg, is reported for surficial materials in Alaska (Gough et al., 2006). Wang and Mulligan (2006) yielded the As range of 4–150 mg/kg in uncontaminated soils of Canada. Elevated As content, up to 732 mg/kg, is reported for Slovakian soils from some locations; however, its background value is given as 7.2 mg/kg (Čurlík and Šefčík, 1999). The range of As in soils of Poland is 0.9–3.4 mg/kg, with the highest value in soils derived from shales.¹³⁵⁷ Chernozems of

TABLE 20.2
Abundance of Trace Elements of Group 15 in Rocks and Soils (mg/kg)

Rock/Soil	As	Sb	Bi
Earth's crust	1.8–2.5	0.2–0.9	0.13–0.2
Igneous Rocks			
Mafic	0.5–2.5	−1	0.001–0.15
Acid	1–2.5	−2	0.01–0.12
Sedimentary Rocks			
Argillaceous	5–13	0.8–4	0.05–0.5
Sandstones	0.5–1.2	0.05	−0.2
Calcareous	1–2.5	0.15–0.3	0.1–0.2
Soils ^a	6.83 ^b	0.67 ^b	0.42 ^b
Arenosols (sandy)	<0.1–30	0.05–1.33	—
Podzols (medium loamy)	1–27	0.05–2	—
Cambisols (heavy loamy)	1–23	0.3–0.6	—
Calcisols (calcareous)	—	—	—
Histosols (organic)	<0.1–67	0.08–0.6	—

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil average (Table 3.2).

western Siberia contain As content from 18 to 32 mg/kg, of which up to 90% is strongly fixed.¹³⁴¹ The As contents in soils of Bangladesh range between 2 and >80 mg/kg (Huq and Naidu, 2005). Commonly, lower As levels are found in sandy soils and, particularly, in those derived from granites, whereas higher As concentrations are related most often to alluvial soils, rich in SOM. Acid sulfate soils are also reported to accumulate a high proportion of As, up to 30–50 mg/kg, in lower horizons.⁹⁸⁴

Ferric hydroxide generally plays an important role in controlling the concentration of As in soils and soil solutions. Anionic forms, AsO_2^- , HAsO_4^{2-} , and H_2AsO_3^- , predominate in soil solutions, although cations As^{3+} and As^{5+} can also occur (Kabata-Pendias and Sadurski, 2004).

1 Reaction with Soil Components

Arsenic behavior in the environment has been broadly reviewed by Bhattacharya et al. (2007). Arsenic minerals and compounds are readily soluble, and arsenopyrite may be easily oxidized by both O_2 and Fe^{3+} . However, As mobility is greatly limited owing to the strong sorption by clays, hydroxides, and SOM. Although As is associated mainly with the heavy mineral fraction of soil, a much higher proportion of total As (27 to 90%) in soils is fixed by the clay granulometric fraction, <0.001 mm.¹⁴²⁷ The positive correlation of As with Fe_2O_3 , the main components of amorphous soil material, indicates its close association with FeO_x (Manaka, 2006). Deschamps et al. (2003) emphasized the function of Mn and Fe minerals in As sorption and Gough et al. (2006) reported its increase, up to 75 mg/kg, in ferricrete sediments in Alaska.

The oxidation states of As are -3 , 0 , $+3$, and $+5$, of which As^0 and As^{3+} are characteristic of reducing environments. As^{3+} is more toxic and mobile in soils than As^{5+} . The complex anions AsO_2^- , AsO_3^{3-} , HAsO_4^{2-} , and H_2AsO_4^- are the most mobile forms of As, being sorbed preferably at the pH range 7–9. The behavior of arsenate (AsO_4^{3-}) resembles that of phosphates and vanadates. Crecelius et al.⁹⁷¹ studied the behavior of As and found that under most environmental conditions, As^{5+} is present as the H_2AsO_4^- species, while As^{3+} as the H_2AsO_3^0 species is only dominant in low pH and low Eh environments. According to Ghosh and Bhattacharyya (2004), OM plays a significant role in As sorption under reduced and reoxidized rise soil condition; however, its sorption is highly controlled by clay content. Violante et al. (2008) concluded that both, arsenates and arsenites, are sorbed primarily by chemisorption at reactive sites of variable charge minerals (e.g., metal oxides, aluminosilicates).

Gustafsson and Bhattacharya (2007) presented geochemical models of As^{3+} and As^{5+} adsorption to oxide surfaces of soil minerals, and to Fe and Al oxides in particular. The authors discussed variable effects of different soil parameters. As speciation in soils is highly governed by its oxidized state. Under common ranges of Eh and pH in soils, the As $+5$ and $+3$ oxidation states predominate. According to Bissen and Frimmel (2003), Eh–pH regime of soil is the most important parameter controlling the As sorption. Elkhabit et al.⁹⁸⁶ stated that oxides and Eh are the main soil parameters controlling the As sorption rate and that the pH of the system influences the concentration of its species being absorbed at the surface of the oxides. Dias et al. (2008) reported that As^{3+} is oxidized on the soil surface and As^{5+} is strongly adsorbed, and also less toxic. Selim and Zhang (2007) evaluated some models for their predictive capability of the As adsorption in soils and suggested that a model versions of multireaction (MRM) is good. Also Szegedi et al. (2007) evaluated usefulness of mathematical models and geochemical code for the description of As dynamics in the rhizosphere.

As ions are known to be readily fixed in soils especially by Fe and Al hydroxides, clay fraction, P and Ca compounds, and SOM. The hydroxy-Al on the external surfaces of micaceous minerals is reported to be especially significant in the retention of As.³²⁹ The strong association of As with Fe (mainly goethite) in soils for both natural As and added As was reported by Norrish.⁵⁷⁰ However, As combined with Fe and Al oxides may be liberated upon hydrolysis with the reduction of soil potential. There are several evidences that As compounds in soils behave like phosphates, and that in acid soils Fe or Al arsenates are likely to be most common.^{570, 887} Complexes of As with P, Fe, Al, and

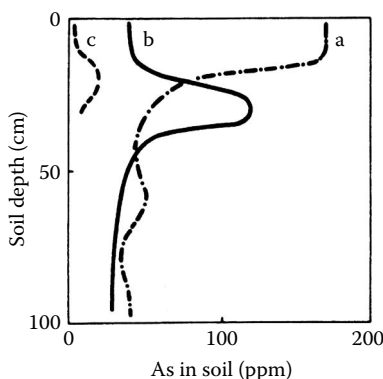


FIGURE 20.1 Patterns of vertical distribution of total As in polluted soils from a nonferrous metal mining area in Japan. (a) Heavy gley soil; (b) light gley soil; and (c) unpolluted paddy soil. (Adapted from Kitagishi, K. and Yamane, I., eds. *Heavy Metal Pollution in Soils of Japan*, Japan Science Society Press, Tokyo, 302, 1981.)

Mn have a significant impact on its behavior in soils (Lund and Fobian, 1991). In acid soils, dominant compounds are Al–As and Fe–As, whereas in alkaline soils predominate Ca–As species.

Dudas⁹⁸⁴ observed that As is associated with both crystalline and amorphous forms of Fe oxides and that vein and spot soil samples enriched in Fe contain As up to 450 mg/kg. According to El-Bassam et al.,²⁰⁴ strongly adsorbed As in soil is unlikely to be desorbed, nevertheless, the retention of As by soil progressed generally with the years.

Since As behavior is dependent on the soil oxidation state, this element varies in its vertical distribution. In heavy gley soil, As is accumulated only in the top horizon and is readily leached from the subsurface layer with a high reduction potential. The As pattern in light well-drained soils is almost the opposite (Figure 20.1). In both contaminated and uncontaminated soils, patterns of As profile distribution may diverge significantly.

Several strains of bacteria accelerate the oxidation of arsenites (As^{3+}) to arsenates (As^{5+}) and are also involved in the As methylation and alkylation. Under anaerobic conditions, As compounds can be reduced, mainly under microbiological processes, to volatile but also easily oxidized to trivalent methylated arsenicals. Microbiota may highly govern the processes of As migration, precipitation, and volatilization as cited by Boyle and Jonasson,⁹⁸ Jernelöv,³⁵⁹ and Weinberg.⁸⁵⁶ Dudas⁹⁸⁴ reported that microbiologically mediated losses of As had depleted topsoils in this element. As Reith and McPhail (2007) reported, microbially mediated release of As was limited and controlled by abiotic adsorption and desorption on Mn- and Fe-oxides.

Microbe-mediated As mobilization was also observed in sediments of shallow aquifers (Guo et al., 2008). The oxidation of As^{3+} to As^{5+} is a fundamental impact of bacteria on the As behavior in soils (Yi et al., 2008). Thus, the biological cycles of As govern its fluxes among the environmental compartments. The biotransformation of organic arsenical pesticides has received recently much attention because their inorganic derivatives may be quite toxic.

Easily mobile As is leached down to groundwater, and creates a great health risk when it is used as a source of drinking water. A disastrous calamity of people suffering from the As intoxication due to As-contaminated waters is well known in West Bengal, India, as well as in several other countries (Samanta et al.,¹⁴⁷⁵ Dangić, 2007; Baciú et al., 2008; Pique et al., 2008; Guo et al., 2008).

2 Contamination and Remediation

Owing to the common As pollution, levels of this element are likely to be increased in topsoils; therefore, sometimes, As ranges reported as background values are also given for contaminated soils. The As content of certain contaminated soils has already been built up to above 2000 mg/kg

TABLE 20.3
Arsenic Contamination of Surface Soils (mg/kg)

Site and Pollution Source	Maximum or Range of Content	Country	Reference
Mineralized bedrock	727	Great Britain	915
Nonferrous metal mining	90–900	Great Britain	144
	3070–11,500	Poland	Karczewska et al. (2007)
Metal-processing industry	130 ^a	Czech Republic	1083
	33–2000	Canada	480, 777
	2500	Great Britain	959
	38–2470	Japan	336, 767
	69 ^b	Hungary	328
	72–340 ^c	Norway	447
	150–2000	Poland	1173
	10–380	United States	153, 538
Chemical works	10–2000	Hungary	328
Application of As-pesticides	10–290	Canada	98, 585
	38–400	Japan	303
	31–625	United States	208, 279, 887
Coal combustion	800–1500	Slovak Republic	1221
Leather industry	105–220 ^d	Germany	1307

^a Data from Maříková.¹⁰⁸³

^b EDTA soluble.

^c HNO₃ soluble.

^d In deeper soil layers.

(Table 20.3). Significant anthropogenic sources of As are related to industrial activities (metal processing, chemical works based on S and P minerals, coal combustion, and geothermal power plants) and to the use of arsenical sprays, particularly in orchards. According to Lazo et al. (2007), As enrichment in soils is mainly associated with Fe–S, Cu–S, and Ni–S mineralization. Bioavailability of As from soils of an abandoned mining area (at the concentration up to 17,400 mg/kg) was relatively low, and the highest (up to 960 mg/kg) was by earthworms (Gal et al., 2007). According to Kitagishi and Yamane,³⁹⁵ the As contamination of paddy soils resulted from both high sorption capacity of these soils and the As transportation by irrigation water. Its extensive use in insecticides for orchards resulted in elevated concentrations in soils, within the range 366–372 mg/kg (Violante et al., 2008).

Forms of As from all sources, for example, irrigation waters, industrial wastes, and pesticides (especially Pb-arsenates and Cu-acetate-arsenates) may need decades to get converted into nonphytotoxic forms in soils. The EU Community recommends that As in agricultural soil fertilized with sewage sludge should not exceed 20 mg/kg, whereas in the United Kingdom, the permissible level is 50 mg/kg (Stoeppler, 2004). The maximum allowable limit of As in paddy soils is proposed as 15 mg/kg.³⁹⁵

Heavily As-polluted garden soils (up to 200 mg/kg As) are reported to be located in the vicinity of a former As smelter.¹⁵²⁸ Thornton and Farago¹⁵¹⁶ reviewed soil As distribution in garden soils, and reported As contents up to about 15,000 mg/kg. However, only a limited fraction of the total amount of As is easily mobile, and over 80% is strongly associated with Fe and Al oxides and is not available for plants. Tjihuis et al. (2007) reported that up to 50% of the As in topsoils of playgrounds is in exchangeable, carbonate, and reducible fractions. They concluded that only sand with no detectable levels of As may be used in sandboxes at playgrounds in Norway.

The As mobility in soil was shown to be proportional to the As added and inversely proportional to time and to Fe and Al contents. According to Violante et al. (2008), some anions reveal an affinity to mobilize As in soils, and their effectiveness follow the order: $\text{PO}_4 \gg \text{CO}_3 > \text{SO}_4 \sim \text{Cl}$. The toxicity of As depends on the concentration of soluble As; therefore, sodium arsenate and arsenic trioxide, formerly used as herbicides, are the most toxic. However, plant growth response may also be related to the total soil As (Figure 20.2). Phytotoxicity of As is highly dependent on soil properties; while in heavy soil about 90% growth reduction appears at 1000 mg/kg As addition, in light soil 100 mg/kg As is equally toxic.⁸⁸⁷

The toxicity of As in soils may be overcome in several ways, depending on As pollution sources and on soil properties. Increasing the oxidation state of flooded (paddy) soils limits As bioavailability.³⁹⁵ Xie and Huang¹⁵⁵⁷ reported that without adding any material to As-polluted paddy soils, wetting and drying greatly increased the soil redox potential and therefore lowered solubility, and phytoavailability, of As to rice plants. Application of materials that produce precipitates with As in soil (e.g., ferrous sulfate, calcium carbonate) is reported to be effective when added to soils having less than 10 mg/kg of soluble As (in 0.05 N HCl).³⁰³ Also, fertilizing, mainly the application of phosphates, decreases the As bioavailability. However, the literature on phosphate retention of As in soils is confusing, for phosphates could also displace adsorbed or fixed As from sorbing complexes and thereby initially increase the amount of soluble As in soils. As Peryea¹⁴⁵⁴ found, a popular fertilizer (monoammonium phosphate, MAP) used on soils contaminated with Pb–As pesticide residues can enhance As solubility, and thus increase As phytoavailability. The alleviating effect of the S application on As toxicity has also been observed. Chandra Sekhar et al. (2007) reported that the addition of Zn and Cd decreases the As uptake by *Talinum cuneifolium*, while some anions (carbonates, acetates, and phosphates) increase its uptake.

According to Kumpiene et al. (2008), the As stabilization in soils occurs through the adsorption of FeO_x by replacing the surface hydroxyl groups with Al ions, as well as by the formation of amorphous Fe^{3+} arsenates and insoluble secondary oxidation minerals. Fe-plaque formed on rice roots in the submerged soil environments reveals a high affinity to bind As^{5+} and thus to control its uptake (Liu et al., 2006).

Hartley and Lepp (2008) reported that FeO_x applied either as minerals (goethite) or as compounds (Fe-bearing materials) reduce the As bioavailability. Nair et al. (2007) described a high efficiency of siderophores for the As removal from contaminated soils. Muller et al. (2007) discussed different leaching procedure for the As mobilization; however, owing to its strong binding in most soils, these procedures may mobilize less than 20% of the total As content.

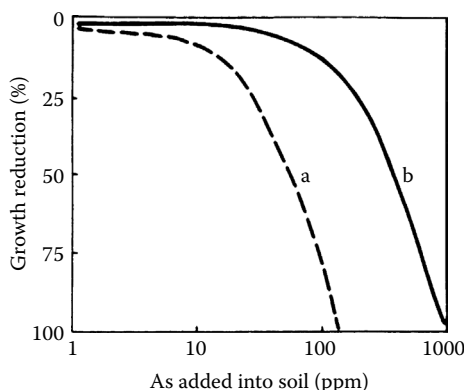


FIGURE 20.2 Corn growth response to As added to two soils. (a) Light soil with low OM content and with kaolinitic clay predominating; (b) heavy soil with high OM content and with vermiculitic clay predominating. (Reproduced from Woolson, E. A., Axley, J. H., and Kearney, P. C., *Soil Sci. Soc. Am. Proc.*, 37, 254, 1973. With permission.)

White lupin was used for the phytostabilization of inorganic contaminants and for As accumulation in roots (Vazquez, 2008). The need for bioremediation technologies for As-contaminated sites has been discussed by Wang and Mulligan (2006).

C PLANTS

Several reports on the linear relationship between As contents of vegetation and concentrations in soils of both total and soluble species suggest that plants take up As passively with the water flow. Some plants, particularly Douglas fir, show a remarkable ability to take up As, far more than many other plants.^{624,851} Thoresby and Thornton⁷⁸³ described the ready uptake of As by various plant species (Figure 20.3). With increasing soil As, high As concentrations were always recorded in both old leaves and roots, but at a low content of As, a higher accumulation in leaves than in roots was reported (Tlustos et al.¹⁵¹⁹). According to these authors, the uptake of As by radish depends on the As species and follows the order: $As_{org} > As^{5+} > As^{3+}$.

Concentrations of As in plants grown in uncontaminated soils vary from 0.5 to 80 $\mu\text{g/kg}$ (Table 20.4). According to Greger (2008), As contents vary significantly in various wheat grains as follows (in $\mu\text{g/kg}$): (1) in winter spelt grains, 18; (2) in bread wheat grains, 40–90; and (3) in durum wheat grains, 175–500. Williams et al. (2007) investigated the As assimilation by grain crops and observed that always it was greater for rice than for wheat or barley.

Several plant species are known to tolerate a high level of As in tissues. The As toxicity has commonly been noted in plants growing in mine waste, soils treated with arsenical pesticides, and soils with As added by sewage sludge treatment. Symptoms of the As toxicity are variously described as leaf wilting, violet coloration (increased anthocyanin), root discoloration, and cell plasmolysis. The most common symptom, however, is a growth reduction. Kitagishi and Yamane³⁹⁵ reported that rice grown in apple orchard soil containing 77 mg As/kg produced almost no yield in the first year. The toxic effect of As was partly reduced after 3 years of cultivation without any special treatment, but an application of S greatly limited the phytotoxicity of As.

Wallace et al.⁸⁴⁵ showed that bush bean plants grown in solution culture with As at 10^{-4} M/L accumulated approximately 4, 19, and 42 mg/kg As, respectively, in leaves, stems, and roots, causing considerable damage. Decreased Mn, P, and Ca concentrations in all plant parts, and K in roots, were reported. As is known as a metabolic inhibitor; therefore, yield reduction of vegetation under a high level of bioavailable As should be expected. Apparently, As is less toxic when plants are well supplied with P. Si seems to inhibit the As toxicity to mitochondria of the rice cells.⁹¹⁹

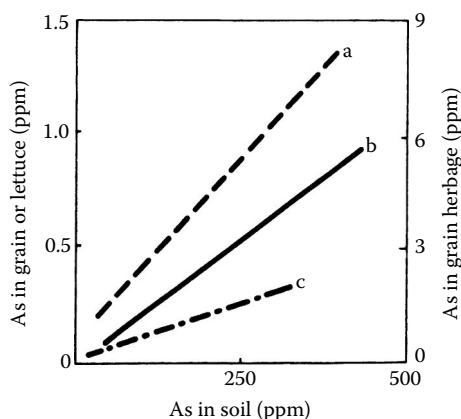


FIGURE 20.3 Concentration of As in plants as a function of total soil As. (a) Lettuce; (b) pasture herbage; and (c) barley grains. (From Thoresby, P. and Thornton, I., *Trace Subst. Environ. Health*, Vol. 13, University of Missouri, Columbia, MO, 93, 1979. With permission.)

TABLE 20.4
Arsenic Content of Food and Forage Plants from Various Countries^a (µg/kg)

Plant	Sample	Range/Mean
Barley	Grains	3–18
Oats	Grains	10
Wheat	Grains	3–10
Rice	Grains	0.5–10
Corn/maize ^b	Grains	1848
Snap beans	Pods	1.3–7
Cabbage	Leaves	20–69
Lettuce	Leaves	20–50
Carrot	Roots	10–80
Potato	Tubers	10–20
Potato ^b	Tubers	864
Tomato	Fruits	9–12
Orange	Fruits	11–50
Edible mushroom	Whole	280
Clover	Tops	20–160
Grass	Tops	280–330 1000–5400 ^c

^a Presented are common, possible background values from various sources, unless otherwise indicated.

^b Plants from Chile, after Queirolo et al. (2000).

^c Grass from climatic zone (Kazakhstan).¹¹³¹

Gough et al.²⁷⁹ reviewed findings on the As phytotoxicity and reported that its content of injured leaves of fruit trees ranged from 2.1 to 8.2 mg/kg. In general, the tolerance for As of agronomic crops is established at 0.2 mg/kg (FW) and in other plants at >5 mg/kg (Table 5.4). However, the critical value in rice plants is as high as 100 mg/kg in plant tops and 1000 mg/kg in roots.³⁹⁵ Davis et al.¹⁷¹ gave the critical As value of 20 mg/kg for barley seedlings, whereas Macnicol and Beckett¹⁰⁸¹ estimated the commonly reported critical upper levels for 10% depression of the yield of various plants to range from 1 to 20 mg/kg.

Excessive uptake of As, in both forms, as arsenites and arsenates, is toxic to plants, reacting with many enzymes and also decoupling P flow in the plant systems (Dixon, 1997). The inhibition of root growth and its ultimate death was also cited under the As stress (Meharg and Macnair, 1991). The availability of As to ray grass (*Lolium perenne* L.) is reduced by compost with 5% of FeO_x and/or 5% of zeolite (Gadepalle et al., 2008). The As availability might be reduced by FeO_x that precipitates in the rhizosphere on root surfaces, whereas chelating ligands (e.g., HIDS, EDTA, EDDS) are likely to accelerate the As phytoavailability (Rahman et al., 2008). Also Voegelin et al. (2007) observed that the accumulation of As in the rhizosphere attenuates its leaching from riparian floodplain soils.

Some plants can be resistant to As excess (e.g., *Holcus lanatus*, *Calluna vulgaris* and *Silene vulgaris* (Meharg, 1994; Sharples et al., 2000). Armienta et al. (2008) described two As-tolerant plants, grown near tailings and smelter slags in nonferric mining area, in the substrates with the As up to 32,000 mg/kg. Plants, mesquites (*Prosopis laevigata*), and huzaiches (*Acacia farnesiana*), accumulate As in twigs up to 82.7 and 225 mg/kg, respectively. According to the authors, these plants might be useful for the phytoremediation. It was also observed that the reduction of arsenate to arsenite in plants may trigger methylated species causing oxidative stress, as reported

TABLE 20.5
Excessive Levels of Arsenic in Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant/Sample	Range/Mean	Country	Reference
Mining or mineralized area	Douglas fir, stems	140–8200 ^a	Canada	851
	Grass, tops	460–6640	Great Britain	624
Metal-processing industry	Grass	0.5–62	Canada	777
	Tree foliage	27–2740 ^b	Canada	480
	Rice, leaves	7–18	Japan	395
	Hay	0.3–2.6	Norway	441
Battery manufacturer	Tree foliage	16–387 ^b	Canada	480
Sludged or irrigated field	Brown rice	1.2 (max.)	Japan	336
Application of arsenical pesticides	Turnip, roots	1.08	Canada	138
	Potato, tubers	1.10	Canada	138
	Carrot, roots	0.26	Canada	138
Various sources	Long bean	2.83	Bangladesh	Huq and Naidu (2005)
	Potato, tubers	2.43		

^a AW basis.

^b Washed leaves.

for some fungus (*Scopulariopsis brevicaulis*) and for phosphate-starved tomato plants (Zaman and Pardini, 1996). Ma et al. (2001) reported that Chinese brake fern (*Pteris vittate*) easily uptakes As from soils and reveals a potential to clean up As-contaminated soils.

The crucial problem in Bangladesh is rice cultivated in irrigated fields. Rice needs 1000 mm of irrigation water per a growth season; the load of As with this water varies between 1.36 and 5.5 kg/ha/year, whereas winter wheat needs only 150 mm water what resulted in the addition of As between 0.12 and 0.82 kg/ha/year. Rice and wheat accumulate As from soils and waters in the following order: (mean values in mg/kg): root, 23 > stem, 4 > leaf, 1.5 > grain, 0.2 > husk, 0.1 (Huq and Naidu, 2005). According to Khan et al. (2005), rice yield decreases with increased As concentration in irrigation water. These authors presented the order of As concentrations in different parts of rice as follows (in mg/kg): rice straw, 2.74–24.9 > rice husk, 1.0–2.72 > rice grain, 0.26–1.23. The problem of As in groundwater used for irrigation is also serious in several other regions, where the As level in waters is increased.

Depending on the location and pollution source, plants may accumulate extremely large amounts of As—above 6000 mg/kg and above 8000 mg/kg AW (Table 20.5). Although As poisoning from plants to animals is believed to be very uncommon, unfavorable health effects of such a high As concentration in vegetables and in forage plants cannot be precluded. According to McSheehy and Szpunar,^{1411a} some sea plants are likely to concentrate a great proportion of As from waters. Predominant As species in sea plants, the so-called “arsenosugars,” are easily converted in the human body to dimethylarsinic acid, which has carcinogenic potential.

II ANTIMONY

A INTRODUCTION

The average content of Sb in the Earth’s crust is estimated as 0.2 mg/kg (Table 3.2). It is a little bit more concentrated in argillaceous sediments (up to 4 mg/kg) than in any other rocks (Table 20.2). The geochemical characteristics of Sb are closely related to those of As and, in part, to those of Bi. Sb usually occurs at the valence of +3 and occasionally of +5 (Table 20.1), and shows amphoteric

behavior. It has chalcophilic properties and is often associated with ore deposits of sulfide of other metals.

Common Sb minerals are stibnite, Sb_2S_3 , and valentinite, Sb_2O_3 . It may substitute for As in several minerals such as pyrrargyrite, Ag_3SbS_3 , and bournonite, $\text{PbS.Cu}_2\text{S.Sb}_2\text{S}_3$. It also easily forms soluble anionic thiocomplexes, such as SbS_2^- and SbS_4^{3-} . The Sb is associated with over 100 Sb-bearing minerals and therefore its increased levels are observed in several industrial regions, specially around smelters, and mining, particularly near deposits of Cu, Ag, and Pb ores.

The Sb is concentrated in some coals, and carbonaceous shales, and is associated with Fe and Mn hydroxides.

The global production of Sb was estimated as 165 kt in 2008 (USDI, 2009). The main source of Sb is stibnite, Sb_2O_3 . It is also recovered from primary concentrates, recycled scrap, and antimonial Pb-battery scrap. The Sb increases the strength and hardness of Pb alloys and is used as an alloying element for Pb-acid batteries. The metal is used for the manufacturing of flame-retardant synthetic fibers.

Recently, Sb and its compounds are considered by the US EPA and the EU to be serious pollutants and its concentration in sewage sludge is recently of a concern (Filella et al., 2002). Especially Sb released from coal combustion is of environmental concern due to its high solubility and reactivity. Shoty et al. (2005) suggested that the influence of anthropogenic factors on the natural flux of Sb to the global atmosphere is underestimated.

B SOILS

The mean background Sb levels of soils of various countries range from 0.25 to 1.04, and average 0.67 mg/kg. Its contents do not differ much between soil groups, but it shows a tendency to be concentrated in Cambisols (Table 20.2).

The reactions of Sb during weathering are not yet well known, it often occurs in soluble forms, some of which are complexed with humates. The Sb is easily adsorbed and thus becomes enriched in clay sediments and in hydrous oxides. Isotopic study shown that ^{125}Sb applied to soil moves readily down the profile.^{1042a} However, other data indicated that Sb is slightly mobile in soils since it is fixed to particles with Fe, Mn, and Al. It is also adsorbed when dissolved as oxyanions, especially at low pH values (Filella et al., 2002). Manaka (2006) confirmed the positive correlation between amounts of amorphous materials and Sb concentration. According to Hou et al. (2006), Sb is mainly (34%) associated with a residual fraction and slightly (6.1%) with a carbonate-bound fraction. Sb occurs in soils mainly as sulfide species (SbS) and thus is slightly phytoavailable, within the range of 0.06–0.59% of its total content (Hammel et al., 2000). Jonet et al.^{1042a} emphasized that biomethylation of Sb may have an impact on its behavior in soils.

The background mean level of Sb in agricultural soils of Sweden is 0.25 mg/kg (Eriksson, 2001), whereas its mean content in contaminated acid sandy soil of Great Britain is 0.7 mg/kg (Ainsworth et al., 1990). In Japanese soils its median contents vary from 0.7 to 1.0 mg/kg, for Cambisols and Acrisols, respectively (Takeda et al., 2004), and averages 0.83 mg/kg (Hou et al., 2006). The 90th percentile for the total Sb in Finnish soil is 0.6 mg/kg (Köljonen¹³⁶⁸). Govindaraju¹³¹³ reported that Sb in reference soils of China ranges from 0.5 to 60 mg/kg (mean 3.6) and Sb in reference soils from the United States ranges from 0.11 to 14 mg/kg (mean 2.4). In the United States (Idaho State) soils, Sb ranges from 2.3 to 9.5 mg/kg (Flynn et al., 2003). High Sb content, up to 247 mg/kg, is reported for soils of some sites of the Slovak Republic; however, its background value is given as 0.7 mg/kg (Čurlik and Šefčík, 1999).

Antimony may be associated with nonferrous ore deposits and is likely to be a pollutant in industrial environments. The increased level of Sb to about 200 mg/kg was found in soils near a Cu smelter,¹⁵³ and elevated air concentrations of Sb have been reported for different smelter operations and urban areas.²¹⁰ Soils from battery reclamation sites are reported to contain up to 857 mg/kg Sb,¹¹⁶⁶ whereas forest soils surrounding a metal smelter in the Czech Republic accumulated in A_0

horizon only 11 mg Sb/kg.¹⁰⁸³ The mobility and leaching of Sb from stibnite mineral, near a Sb smelter in New Zealand, were observed (Wilson et al., 2004). Also, Ashley et al. (2003) confirmed the mobility of Sb in Fe-free or Fe-low systems. In soils surrounding Sb smelters and mining areas, it is mainly bound to Fe–Mn-oxides and OM. The Sb mobile species range between 0.007 and 0.03 mg/kg and do not show any association with pH (Li and Thornton, 1993). Casado et al. (2007) reported a low mobility of Sb, within the range of 0.02–0.27% of the total Sb in soils containing 60–230 mg As/kg. High Sb level in soils near industrial sites decreases with depth, which indicates that it is rather nonreactive and mostly immobile and will not contaminate the groundwater (Hammel et al., 2000). Studies of Nakamaru et al. (2005) show a very low mobility and reactivity of Sb in Japanese soils. Muller et al. (2007) used different leaching procedures that mobilized less than 20% of the total Sb content due to its strong binding to soils. However, its easy solubility in a citric acid solution from mine-waste-contaminated soils indicates its relatively easy phytoavailability (Telford et al., 2008). Bioavailability of Sb from soils of an abandoned mining area (at the concentration up to 1200 mg/kg) was relatively low, and the highest (up to 27 mg/kg) was by earthworms (Gal et al., 2007). The contamination with Sb is often reported, mainly for soils at hazardous waste sites and at Sb-processing sites. Data presented by Flynn et al. (2003) and other authors gave the following high concentrations of Sb in topsoils (in mg/kg):

- 65–109; Cu smelter, the United States, East of Tacoma
- 49–204; Cu smelter, the United States, Maury Island
- 280; Au refining, the United States, Yellow Knief
- 360; Sb smelter, the United Kingdom
- 1565; Sb-mining areas, China (He and Yang, 1999)
- 109–2550; various Sb smelters (ATSDR, 2002)
- 10–1200; abandoned mining area, Scotland (Gal et al., 2007)

C PLANTS

Although Sb is considered a nonessential metal, it is relatively easily taken up by plants if present in soluble forms. There are some recent data on Sn impacts on plants. Picard and Bosco (2006) observed increased auxin production by rhizobacteria with increased soil Sb concentration. According to Feng et al. (2009), some antioxidative enzymes (peroxidase, catalase, and ascorbate peroxidase) might be involved in the Sb toxicity resistance of fern (*Pteris cretica*), but not of other fern plants.

There are variable data on Sb in plants. As Bowen⁹⁴ reported, the Sb mean content of terrestrial plants is 60 µg/kg. Oakes et al.⁵⁷⁴ gave the range of Sb concentrations in edible plants as 0.02–4.3 µg/kg FW, with cabbage being in the upper range and apple fruits in the lower range. Commonly reported Sb contents in agricultural plants range from <2 to 29 µg/kg, and usually its contents in plants decrease in the following order: roots > leaves and shoots > grains. However, there are some data for a very high Sb level in spinach leaves (Table 20.6). Ozoliniya and Kiunke⁵⁸⁸ showed that the Sb content of barley and flax roots was, 122 and 167 µg/kg, respectively, and exceeded that of leaves having 10 and 27 µg/kg. The same plants grown in peat soil contained several times less Sb in roots, while the concentration in leaves was about the same as that given above.

The Sb concentration vary from <20 to 1130 µg/kg in food plants that grown in soils of historical mining areas (Table 20.6). In these soils, Sb occurs mainly in sulfide form, SbS, that is slightly phytoavailable, at the range of 0.06–0.59% of the total Sb content (Hammel et al., 2000).

There are no reports on plant toxicity caused by Sb. Only results of the experiment carried out by He and Yang (1999) show that Sb³⁺, at the highest dose (1000 mg/kg), reduced significantly the yield of rice, in the pot experiment, as compared with the impact of the Sb⁵⁺ addition.

The Sb levels in Norwegian mosses sampled in 1995 range 8.3–4300 µg/kg (average, 150) and do not reflect any significant effect of aerial pollution.¹²²³

TABLE 20.6
Antimony Content of Food and Forage Plants from Various Countries ($\mu\text{g}/\text{kg}$)

Plant	Sample	Range/Mean
Barley ^a	Grains	1
Wheat ^a	Grains	0.5
Corn ^b	Grains	<2
Oats ^c	Grains	<20–60
Potato ^c	Tubers	<20–20
Parsley ^c	Roots	50–420
Spinach ^c	Leaves	150–1130

^a After Eriksson (2001).

^b After Laul et al.⁴⁶²

^c Data for plants from historical mining areas, after Hammel et al. (2000).

III BISMUTH

A INTRODUCTION

Bi is considered a rare metal in the Earth's crust (mean 0.2 mg/kg) and is usually found in veins associated with some metals (e.g., Ag, Co, Pb, Zn). Its higher concentrations in argillaceous sediments do not exceed 0.5 mg/kg (Table 20.2). Its oxidation stages are +3 and +5 (Table 20.1), and may be a strong oxidizing agent.

Bi reveals both chalcophilic and lithophilic properties. During weathering, it is readily oxidized, and when it becomes carbonated (e.g., as $\text{Bi}_2\text{O}_2\text{CO}_3$), it is relatively stable. Its common minerals are bismuthinite, Bi_2S_3 ; and bismite Bi_2O_3 . Possible host minerals are galena, sphalerite, and chalcopyrite. Its accumulation in coals and in graphite shales is reported to average at about 5 mg/kg.

The annual world production of Bi in 2008 was estimated as 5.8 kt (USDI, 2009). It is associated with several ores (e.g., Cu, Hg, Sn, Ag, Au, W) and is often obtained as a by-product of various ore processing, mainly of Pb ores (in the United States), and of W ores (in China).

Bi is broadly used in low-melting alloys, fuses, sprinklers, glass, and ceramics production, and also as a catalyst (e.g., rubber production). It is also used in some metallurgical industries, as well as in different electronic devices. As a nontoxic replacement for Pb, Bi is used in several food-processing equipments and recently in pellets.

At the +5 oxidation state, Bi is a strong oxidation agent (e.g., NaBiO_6 or BiF_5). Due to its versatile properties, it is used in pharmaceutical and cosmetic production, as well as in dentistry and medicine.

B SOILS

The Bi content of surface soils is directly inherited from parent material and averages 0.42 mg/kg (Table 3.2). Bi reveals chalcophilic properties, but during weathering, it gets readily oxidized, and when it becomes carbonated (e.g., $\text{Bi}_2\text{O}_2\text{CO}_3$), it is very stable in soils.

There is a paucity of data on the Bi contents of soils. Ure et al.⁸¹⁹ reported the mean Bi content of arable Scottish soils derived from different rocks to be 0.25 mg/kg (range, 0.13–0.42). According to Chattopadhyay and Jervis,¹³² the Bi range in garden soils of Canada is 1.33–1.52 mg/kg. The Bi contents in reference soils of China range from 0.04 to 1.2 mg/kg and Bi contents in reference soils of the United States is within the range 0.03–0.69 (Govindaraju¹³¹³). The background Bi content in Slovakian soils is given as 1.3 mg/kg, but elevated concentrations, up to 37.2 mg/kg, are also noticed (Čurlik and Šefčík, 1999). Aubert and Pinta³⁹ reported Bi in ferrallitic calcareous soils of Madagascar

to be 10 mg/kg. Japanese soils contain, at average, 0.32 mg Bi/kg, of which the highest proportions were fixed by amorphous MeO_x (26%) and SOM (26%); (Hou et al., 2006). Tyler and Olsson (2005) observed an increased Bi level (92 mg/kg) in raw humus soils as compared with ectomycorrhizal beech roots (12 mg/kg). Manaka (2006) reported the positive correlation between Bi and FeO_x in amorphous material from a brown forest soil. Thus, an increase of Bi in soil horizons rich in FeO_x and SOM should be expected.

Sewage sludge and fertilizers, phosphates in particular, are often significant sources of Bi in soils. Eriksson (2001) gave the following Bi concentrations in materials used for soil amendments (in mg/kg): (1) sewage sludge, 0.73; (2) manure, 0.72; (3) NKP-fertilizers, 0.02; and (4) P-fertilizers, 0.18.

Bi pellets used recently (since 1997) in Canada instead of Pb pellets increased the Bi levels in soils, up to a mean content of 2.55 and 6.40 mg/kg in acidified and nonacidified soils, respectively (Fahey et al., 2008).

C PLANTS

The Bi content of plants has not been studied extensively. Shacklette et al.⁷¹⁰ reported that Bi was found only in about 15% of a number of samples of Rocky Mountain trees and that the Bi range was from 1 to 15 mg/kg AW. Bowen⁹⁴ gave the mean Bi as $<20 \mu\text{g/kg}$ in land plants and 0.06 mg/kg in the edible parts of vegetables. Erämetsä et al.²¹⁶ found a range of Bi in *Lycopodium* sp. from <1 to 11 mg/kg, with about 60% detectability. Bi is likely to be concentrated in plants from polluted sites, mainly due to coal combustion and sewage sludge. Berg and Steinnes¹²²³ found that Bi content ranges from 1 to 800 $\mu\text{g/kg}$ (average, 33) in Norwegian mosses collected in 1995. Aboveground tissues of *Cares lagustris*–*Agrostis scabra* community from plots receiving Bi pellets contained this element within the range of 65–95 $\mu\text{g/kg}$, but often its content was below detection levels (57 $\mu\text{g/kg}$) (Fahey et al., 2008).

21 Elements of Group 16 (Previously Group VIa)

There are only two stable elements in Group 16: selenium (Se) and tellurium (Te). Both resemble S in a number of geochemical properties; however, their behavior in the environment is more complex. Polonium (Po), natural isotope of the U–Ra transformation chain, also belongs to this group. These elements, which are nonmetals, but also considered metalloids, are highly mobile in the Earth's crust and reveal both chalcophilic and siderophilic properties. All of these elements exist in variable valence states from -2 to $+6$ (Table 21.1).

I SELENIUM

A INTRODUCTION

The average content of selenium in the Earth's crust is estimated as 0.05 mg/kg; however, a higher value, up to 0.5 mg/kg, is also given. It is slightly more concentrated in mafic rocks, but rarely exceeds 0.1 mg/kg (Table 21.2). In sedimentary rocks, Se is associated with the clay fraction and thus its abundance in argillaceous sediments (0.3–0.6 mg/kg) is higher than in sandstones and limestones (0.01–0.1 mg/kg). Enriched Se concentration in Cretaceous rocks (up to above 100 mg/kg) was derived from volcanic gases and dust brought down by rain into the Cretaceous sea; thus sediments of that period are likely to be enriched with Se. Some sedimentary rocks formed in nonvolcanic periods also may be enriched with Se, probably in a normal course of weathering.

Selenium is allotropic and may occur in three crystallic forms and two amorphous ones. Due to close crystallochemical behaviors of Se and S, much of the Se geochemistry is close to the more abundant S. It reveals complex behavior in geochemical processes that resulted from relatively easy changes of its oxidation states. The easy methylation of Se, mainly due to biological processes, yields the formation of volatile Se forms and has a significant role in the biogeochemical cycling of this element.

Selenium exists in four valence states, of which the -2 state predominates in organic Se compounds. Commonly occurring species, selenites (Se^{4+}) and selenates (Se^{6+}), in geochemical environments do not form stable compounds and are preferably absorbed by minerals, particularly clay minerals, and Fe and Mn oxides and hydroxides.

Approximately 50 Se minerals are known, of which the relatively common ones are: klockmanite, CuSe ; berzelianite, Cu_{2-x}Se ; clausthalite, PbSe ; tiemannite, HgSe ; ferroselenite, FeSe_2 and crookesite, $(\text{Cu}, \text{Tl}, \text{Ag})_2\text{Se}$. The association of Se with host minerals, such as pyrite, chalcopyrite, and sphalerite, is relatively common.

The great affinity of Se to different organic substances resulted in a large number of organic compounds that are analogous to those of S organic compounds and are easily accumulated in some biolithes. Its concentrations (in mg/kg) may be up to 10.7 in coal, and up to 1.4 in crude oils and bituminous shales. Extremely high Se concentrations, up to 6500 mg/kg, is in Chinese stone coal (Plant et al., 2004). Se concentrations of as much as about 0.1% are not uncommon in the immediate vicinity of some oxidized sandstone-type uranium deposits. Atmospheric deposition of Se in some regions might be of an environmental concern. Kubota et al.^{436a} calculated that the amounts of Se in rainwater that fall on land surfaces reflect several Se sources such as volcanic exhalations and industrial emissions, in particular, the combustion of coals.

TABLE 21.1
Selected Properties of Trace Elements of Group 16

Element	Atomic Number	Atomic Mass	Atomic Radius ^a (pm)	Density (20°C) (g/cm ³)	Valence ^b
Se, selenium	34	78.96	122	4.26–4.81 ^c	–2, +2, +4 , +6
Te, tellurium	52	127.60	142	6.24	–2, +4 , +6
Po, polonium	84	209 ^d	153	9.32 (alpha)	–2, +4 , +6

^a Approximately average values for the main oxidation states.

^b Valence values in bold are for the main oxidation states.

^c Range of various Se species.

^d Average atomic mass.

Global Se production in 2008 was calculated as 1.59 kt (USDI, 2009). It is a common by-product of copper refining and in the production of sulfuric acid.

The largest use of Se, as a pigment, is in glass and ceramic manufacture. It is used (with Bi) in brasses to replace more toxic Pb. The Se is also used to improve abrasion resistance in vulcanized rubbers. Its use in toning of photographic prints, as well as in various photoelectric cells, is relatively common. In agriculture, Se is used as an addition (mainly as sodium selenite, Na₂SeO₃) to insecticides, fertilizers, and foliar sprays.

Selenium is widely used, in small doses, in vitamins and other dietary supplements. Also some livestock feeds are fortified with this element. It is a relatively common component of various cosmetics and medications, as a therapeutic agent (e.g., in cardiology as an antioxidant). It is one of

TABLE 21.2
Abundance of Trace Elements of Group 16 in Rocks and Soils (mg/kg)

Rock/Soil	Se	Te
Earth's crust	0.05	0.005–0.3
Igneous rocks	—	—
Mafic	0.01–0.12	0.001
Acid	0.01–0.05	0.005
Sedimentary rocks	—	—
Argillaceous	0.3–0.6	<0.01 ^a
Sandstones	0.01–0.08	—
Calcareous	0.03–0.10	—
Soils ^b	0.44 ^c	0.006 ^d
Arenosols (sandy)	0.25–0.35	0.03 ^e
Podzols (medium loamy)	0.05–1.52	—
Cambisols (heavy loamy)	0.18–0.85	—
Calcisols (calcareous)	0.20–1.40	—
Histosols (organic)	0.30–1.50	—

^a Shales.

^b Soil groups are given according to the WBR (Table 3.1).

^c World-soil data (Table 3.2).

^d Mean for world soil, after Reimann and Caritat (1998).

^e Mean values for European soils (FOREGS, 2005).

the elements that play the most important role in human and animal health. Recently, numerous studies have been carried out on this element and this has resulted in a huge number of publications.

B SOILS

The mean total Se content in worldwide soils is estimated as 0.44 mg/kg (Table 3.2). Its background contents of various soil groups range from 0.05 to 1.50 mg/kg, being the lowest in Podzols and the highest in Histosols (Table 21.2).

Soil Se is inherited from parent material and its distribution highly reflects soil-forming processes and also atmospheric deposition. Averages (background) levels of Se in sandy soils (mainly Podzols) are reported for some countries at values of (in mg/kg): (1) 0.21, Finland (Eurola et al., 2003); (2) 0.14, Lithuania (Antapaitis et al., 2004); (3) 0.14, Poland (Kabata-Pendias and Pendias¹³⁵⁷); (4) 0.18, Russia (Jermakov and Kovalskiy³⁵⁸); (5) 0.23, Sweden (Eriksson, 2001); (6) 0.50, the United States (Lakin and Davidson⁴⁵⁴); (7) 0.10, Slovakia (Čurlik and Šefčík, 1999); and (8) <0.2–>3, various soils of Japan (Oldfield, 2002).

The Se content of soils has received much attention mainly in countries where the role of Se in man and animal health has been widely recognized. Most soils of the temperate humid climate zones, and derived from sedimentary rocks contain low Se levels that are not sufficient to produce food and fodder plants with adequate Se contents. The application of farmyard manure is reported to be a good means of increasing Se levels in Se-deficient soil.¹²²⁹

The program of increasing the Se status of soils in Finland began in 1984. It was based on the Se (as sodium selenate) addition to inorganic fertilizers at levels ranging from 6 to 10 mg/kg, with a permitted highest concentration of 15 mg/kg (Eurola et al., 2003). The mean hot-water extractable Se in soils before this program (in 1979) was 0.006 mg/L, and after the program (in 1998) was 0.01 mg/L. However, Se that was easily available to plants was present only in the first summer after fertilizing, and quickly turned into unavailable forms in the soil. These authors stated that there is not any long-term environmental risk since Se remains in soils as immobile species. Studies of Vuori et al.¹⁵³⁴ indicated that selenates were soluble for at least 3 months after the addition. The sorption of Se was correlated positively with clay content, Fe content, and surface area and negatively with sulfuric acid-extractable P. However, these authors have also stated that the behavior of selenates is not uniform in cultivated soils of Finland, and that added selenates sorbed during the first growing season can later be mobilized into soluble fractions. The Se addition to fertilizers in Finland, during the period 1983–1992, resulted in increasing Se in river waters (up to 180 mg/l), and especially in bottom sediments (up to 3.94 mg/kg).^{1537,1538} Results of this experiment showed that the phytoavailability of the Se added to soils varies significantly, depending on soil parameters.¹⁵³⁴

Elevated concentrations of Se are observed in some ferralsols, organic soils, and other soils derived from Se-rich parent materials (Table 21.5). Also, in salt-affected soil, the total Se, as well as, the water-soluble Se is likely to be elevated.⁷²⁹ There exists a great concern about enriched water-soluble Se levels in soils because increased bioavailability of Se is a direct health risk to human and livestock. The water-soluble Se content of soils is reported to range from 0.2 to 2 µg/kg in the Se-deficient endemic areas in China, whereas in neighboring nonendemic areas, easily soluble Se varies from 1 to 11 µg/kg.¹¹⁸⁹

1 Reaction with Soil Components

During chemical weathering of rocks, Se is easily oxidized and the state of its oxidation, as well as its solubility, is controlled by the pH–Eh soil system. Also, the biological methylation of Se, yielding the volatile Se compounds, is common and plays a significant role in the Se geochemical cycle. Selenite ions resulting from oxidation processes are stable and able to migrate until they are adsorbed on mineral or organic particles. Apparently, selenites are the preferable species of Se being adsorbed

by clay minerals, particularly by montmorillonite and Fe oxides.²⁴⁶ Especially, the adsorption of SeO_3^{2-} by goethite is highly pH dependent.⁹³

A high Se mobility can be expected in soils of high pH and Eh. Controversially, its low mobility occurs in soils with high contents of hydroxides, clay granulometric fractions, and SOM (Table 21.3). In acid soils, Se is likely to occur as Se^{4+} , strongly adsorbed by Fe oxides to form ferric selenite, $\text{Fe}_2(\text{OH})_4\text{SeO}_3$, and iron selenide, FeSe . The maximum Se adsorption occurs between pH 3 and pH 5 and decreases as the pH increases. In alkaline Se-rich soils, predominated species is Se^{6+} , which is very weakly adsorbed. Hence, selenates occur in soluble forms in soil of arid and semiarid regions.

Variable properties and the Se origin resulted in its complex behavior in soil environment. The Se present in soils originates from different sources:

- Lithogenic—parent materials are highly variable in Se content
- Pedogenic—increased content in A and B horizons of soils due to the fixation by SOM, Fe and Mn hydroxides, and clay minerals

TABLE 21.3
Soil Factors Affecting the Mobility of Selenium

Soil Factors	Se Form	Mobility
pH		
High (alkaline)	Selenates	High
Medium (neutral)	Selenites	Moderate
Low (acid)	Selenides	Low
Eh		
High (high oxidation)	Selenites	High
Low (low oxidation)	Selenides	Low
Hydroxides (Fe, Mn)		
High content	Absorbed all forms of Se	Low
Low content		High
Organic Matter^a		
Undecayed	Absorbed	Low
Decayed (e.g., peat)	Complexed	High
Enhanced biomethylation	Volatilized	High
Clays^b		
High content	Absorbed	Low
Low content	Not fixed	High
Interactions		
Sulfur	Antagonistic effects	Rather low
Phosphate		
Nitrogen		

Source: Reproduced from Kabata-Pendias, A. J. *Environ. Pathol. Toxic. Oncol.*, 17, 173, 1998. With permission from Begell House, Inc.

^a Variable impact of organic matter depends on its kind.

^b Absorption by clay minerals decreases with increasing pH values and, at pH 8, is almost negligible.

TABLE 21.4
Impact of Soil pH–Eh System on the Formation of Soluble Se Species

Redox Value (Eh, mv)	pH	Oxidation State of Se	Major Species in Soil Solution
High, >400	7	+6	SeO_4^{2-} selenates
	<2	+6	HSeO_4^-
Moderate, 200–400	>7	+4	SeO_3^{2-} selenites
	<7.3	+4	HSeO_3^-
Low, <200	>3.8	–2	HSe^- selenides
	<3.8	–2	H_2Se^0

Source: After Kabata-Pendias, A., *J. Environ. Pathol. Toxic. Oncol.*, 17, 173, 1998.

- Atmospheric—mainly deposition with rainfall, Se is present in the atmosphere due to volcanic exhalation, industrial emission, methylation, and volatilization from sea and soil surfaces
- Phytogenic—volatilization from plants and soil microorganisms, and burning of seleniferous vegetation
- Anthropogenic
 - *Agricultural*: Se applied to soils, foliar sprays, seed treatments, and P-fertilizers
 - *Industrial*: fly-ash, smelting of some ores, wastes of some ores, some sewage sludge

Based on the Se geochemistry, it seems to be possible to predict trends of Se behavior in a particular soil environment. Elrashidi et al.⁹⁸⁹ studied equilibrium reactions and constants for 83 Se minerals and solution species that relate to soils and observed that the redox potential (Eh) of soils controls the Se speciation in solution (Table 21.4). They described Se species and Se–metal complexes that are likely to occur in soils under various conditions. In soils of high Ca and Mg concentrations, both CaSeO_4 and MgSeO_4 contribute to the total Se in solution, whereas in acid and very acid soils, the most important compounds seem to be KHSe , NH_4HSe , and MnSe . A generalized summary of Se species that may occur in soils is presented in Figure 21.1.

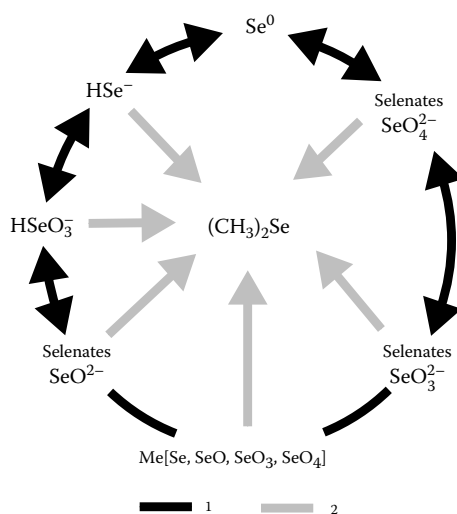


FIGURE 21.1 Ionic species and transformation of Se compounds in soils. (1) Reduction–oxidation; (2) methylation.

Specific properties of Se forms/species are presented by Lakin and Dawidson,⁴⁵⁴ Combs and Combs,⁹⁶⁹ and Frankenberger and Engberg¹³⁰³ as follows:

- Selenates (Se^{6+}) are mobile in inorganic forms in ordinary alkaline soils and are not absorbed on hydrous sesquioxides (especially $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$)
- Selenites (Se^{4+}) are slightly mobile in ordinary neutral or acid soils of humid temperate regions and are easily absorbed on hydrous sesquioxides and SOM
- Selenides (Se^{2-}) are rather immobile in acid soils due to the formation of stable mineral and organic compounds

Selenium can be included in various organic compounds, especially those containing S, and can be sorbed on organic particles as well. The transformation of Se forms in all soil conditions is based mainly on the following processes: (1) selenates to selenites—slow process, and (2) selenites to selenides, to elemental Se, and to organic compounds—very slow process.

Several complex anions of Se, however, as well as organic compounds and chelates, greatly modify the behavior of Se in each particular soil (Table 21.3). This has been nicely illustrated by various trends in Se distribution along soil profiles (Figure 21.2).

The Se solubility of most soils is rather low; therefore, many agricultural areas produce crop plants and forage with a low Se content. However, in naturally Se-enriched soils, in poorly drained or calcareous soils, in soils of aridic zones, and also in soils heavily amended with sewage sludge or fly-ashes, Se may be accumulated by plants in concentrations high enough to be toxic to grazing livestock. Phosphates and sulfates reduce the Se adsorption, especially on Fe oxides, and are effective in releasing and mobilizing up to 90% of the soil-adsorbed selenites and selenates.⁹⁴⁸

It has been estimated that absorbed forms of Se in soil ranges from 15% to 40% of its total contents and that organic Se ranges from 4 to 22% of the total contents.¹³⁵³ Nakamaru et al. (2005a) found that 28–78% of the adsorbed Se was in Al-bound and 14–53% was in Fe-bound fractions. The behavior of Se in highly calcareous soil is of special concern because when soils are low in sesquioxides, the Se becomes easily water soluble. Bar-Yosef and Meek⁹³⁴ observed that the adsorption of Se by clay minerals decreased with elevating pH values and became negligible above pH 8. Singh⁷²⁹ stated that the best effects in correcting the Se toxicity to plants in such soils are obtained by the application of S, P, and even N onto the soils.

The biological methylation of Se occurs in plants and microorganisms as well as in the soil and aquatic environments. Inorganic Se undergoes methylation to gaseous compounds (dimethylselenides). Thus, methylated derivatives of Se are often volatile from soils. On the other hand, a considerable input of Se to soils takes place through the precipitation.

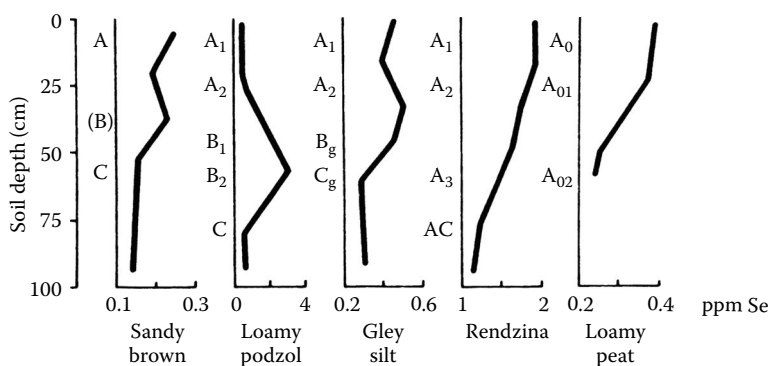


FIGURE 21.2 Distribution of Se in some profiles of soils in New Zealand. (Letters indicate genetic soil horizons). (From John M. K., Chauh, H. H., and van Laerhoven, C. J., *Soil Sci.*, 124, 34, 1977. With permission.)

Forms and concentrations of Se in soil solution are governed by various physical–chemical and biological factors; its common inorganic anions are SeO_3^{2-} , SeO_4^{2-} , HSeO_4^- , HSeO_3^- , and H_2SeO_4^- (Haygarth, 1994; Kabata-Pendias and Sadurski, 2004). Under oxidizing conditions SeO_4^{2-} is the favored form, while in mild reducing conditions, SeO_3^{2-} is likely to dominate. This anion is strongly sorbed on oxides and precipitates as $\text{Fe}(\text{SeO}_3)_3$, whereas SeO_4^{2-} is very weakly sorbed, especially at high pH. Hence, mobile and easily phytoavailable Se occurs in alkaline well-aerated soils, preferably in arid and semi arid regions. OM has a strong tendency to form organometallic complexes and thus removes Se from soil solution.

The water-soluble fraction of soil Se is considered to be the fraction that is available to plants. Van Dorst and Peterson¹⁹⁰ reported the close positive correlation between the Se content of plants and the selenate ion concentration in the soil solution. However, other Se fractions may also be soluble in soils, and thus Elsokkary²¹² concluded that, on average, about 45% of the total soil Se could be available to plants and that plant-available fractions could be extracted with K_2SO_4 or NH_4OH solutions. Soltanpour and Workman⁷⁴⁵ found a good correlation between Se uptake by alfalfa and the Se, which was soluble in DTPA with ammonium acid carbonate. The amount of water-soluble Se in soils varies considerably and does not correlate with the total soil Se. The total Se level is, therefore, a poor predictor of the phytoavailability of the element.

2 Contamination

The phytoremediation has become recently a hot topic of several experiments. For example, elevated concentrations of Se, resulting from irrigation practices, in soils in California (San Joaquin Valley, an area underlain with seleniferous parent material) became a real environmental concern.¹³⁰³ A number of projects are presently under way for remediation and prevention strategies. Phytoremediation seems to be a promising method.^{1367,1450}

The Se toxicity encountered in arid and semiarid regions with alkaline soils requires alleviation. “The green technology of selenium phytoremediation” (Banuelos, 2001) and many other publications provide a broad review on the plant potential (often transgenic plants) to minimize Se loads by uptaking elevated amounts of Se from soils and, partly, by its volatilization (Banuelos et al., 2002; Parker et al., 2003; LeDuc et al., 2004; Van Huysen et al., 2004; Vallini et al., 2005).

Di Gregorio (2008) summarized results of various greenhouse studies and concluded that the total Se concentrations in the soil were at least 20% lower at postharvest compared to preplant Se contents. He also emphasized that rhizobacteria, as well as other microbial activities, have a significant impact on the Se phytoremediation owing to its increasing bioavailability and volatilization.

C PLANTS

Most plants contain rather low Se levels, around 25 $\mu\text{g}/\text{kg}$, and rarely exceed 100 $\mu\text{g}/\text{kg}$. However, some plants reveal a great capability to accumulate Se and they may concentrate Se to extremely high levels that may be toxic to humans and animals. Although Se is not an essential element for plants, with some exceptions, it is being added to soil to ensure that both food and feed products contain adequate amounts for the dietary needs. It should be emphasized that the margin of safety of Se concentrations is rather narrow.

The Se content of crops received recently much attention because of its importance in the food chain. Thus, most data that are available are for food and fodder plants. Especially, cereal grains, as the most common source of Se in diets, have been broadly analyzed. The anticarcinogenic effectiveness of various Se compounds in plants has been recently broadly investigated (Fordyce, 2005; Finley, 2005).

1 Absorption and Transport

The uptake of Se by plants depends on several factors, but when Se is present in soluble forms, it is readily absorbed by plants, although differences between plant species are very pronounced.

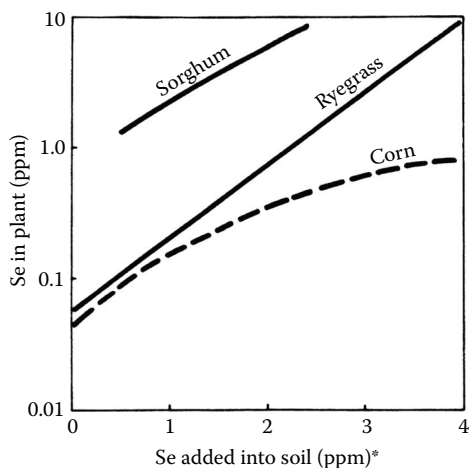


FIGURE 21.3 Influence of Se added as Na_2SeO_3 into the soil on the Se content of plants. *Se level in soil in the experiment with sorghum is given in 10 times lower concentration (e.g., at the range of 0.05 to 0.25 mg/kg). (From Moré, E. and Coppnet, M., *Ann. Agron.*, 31, 297, 1980; Singh, M., *Abstr. 12th Int. Soil Sci. Congr., Part I*, New Delhi, 1982, 412. With permission.)

Di Gregorio (2008) presented a broad review of the Se metabolism in plants and concluded that regardless of the common traits of these processes, different plant capacities to extract and accumulate this element is evidently related to different metabolic strategies. In most cases, there is a positive linear correlation between Se in plant tissues and Se contents of soils. However, the complex impact of variable factors on Se uptake by plants can significantly alter the relation between Se in plants and soils. When present in soluble forms, Se is readily absorbed by plants, although differences between plant species are commonly observed (Figure 21.3). The availability of soil Se is also controlled by several soil factors, among which pH is believed to be the most pronounced (Figure 21.4).

There is a great variation in plants' capability to absorb Se from soils, especially from seleniferous ones. Thus, plants have been divided into three categories: (1) plants that are accumulators and

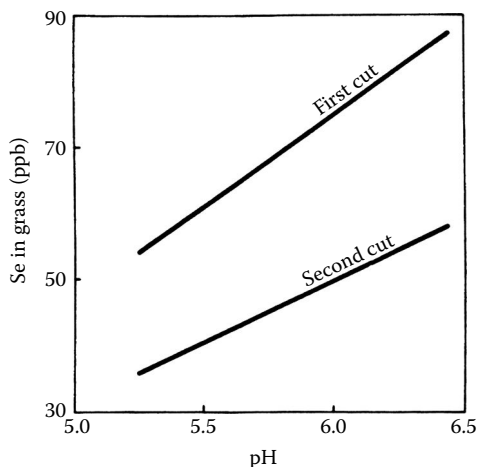


FIGURE 21.4 Se content of ryegrass as a function of the soil pH. (Reproduced from Moré, E. and Coppnet, M., *Ann. Agron.*, 31, 297, 1980. With permission.)

TABLE 21.5
Selenium Content of Surface Soils Derived from Se-Rich Parent Materials (mg/kg)

Country	Soil	Range	Mean	Reference
Great Britain	Peat	92–230	138	880
Ireland	Peat	3–360	54	234
U.S. (South Dakota)	Mineral	6–28	17	454
Armenia	Mineral	0.8–2.2	1.3	358

contain high amounts of Se ($>1000 \mu\text{g/kg}$) and presumably require this element, (2) plants that absorb medium quantities, up to around $100 \mu\text{g Se/kg}$, and (3) plants that are nonaccumulators, containing usually below $30 \mu\text{g Se/kg}$, under field conditions. Plants that can hyperaccumulate Se are species mainly of *Astragalus* and several other herbaceous species, for example, *Oenopsis*, *Stanleya*, *Xylorhiza*, and *Machaeranthera*. These plants can accumulate Se well above $100 \mu\text{g/kg}$ when grown in Se-rich soils, but even when grown in soils of low-to-medium Se contents can accumulate up to $100 \mu\text{g/kg}$. The Se content $>5000 \mu\text{g/kg}$ was reported in certain *Astragalus* species (Streit and Stumm, 1993). Not all plant species grown in seleniferous soils are Se accumulators, and may contain Se only at few $\mu\text{g/kg}$. Variable capability of plants to either concentrate or exclude Se from the growth media is closely related to the complex mechanism of Se compounds transformation and differences in Se pathways (Terry et al., 2000). (Table 21.5)

Selenium is easily absorbed directly from atmospheric deposition that is clearly shown by its high accumulation in both mosses and mushrooms. Mosses from the Scandinavian countries contain Se at an average of $390\text{--}2900 \mu\text{g/kg}$ (Berg and Steinnes¹²²³). Mosses sampled in Germany during the period 1995–96 contained Se in the range of <140 to $>560 \mu\text{g/kg}$, and increased Se concentrations were observed in western and eastern heavily industrialized regions (Oldfield, 2002). High Se accumulation in rootless mushrooms also indicates its ready absorption from atmospheric sources (Table 21.6). Large variation in the contents of Se in mushroom fruiting bodies seems to indicate that neither species nor sites have a significant impact on its absorption. Also, grasses and other monocotyledonous and dicotyledonous plants absorb volatile Se from the atmosphere via the leaf surface. This Se is transported and accumulated in roots in various forms of inorganic selenite,

TABLE 21.6
Mean Selenium Content of Mushrooms from Some European Countries^a (mg/kg)

Mushroom Species	Finland	Norway	Poland ^b	Switzerland ^b
<i>Boletus edulis</i>	17	—	8.7–23 ^c	14; 13
<i>Macrolepiota procera</i>	4.8	—	4.9	2.4; 0.7
<i>Agaricus compestris</i>	2.7	2.9	5.9	5.7; 3.6
<i>Leccium testaceoscabrum</i>	0.6	1.3	1.1; 6.9	1.2
<i>Lactorius deliciosus</i>	0.9	—	2.0	1.2; 0.6
<i>Cantharellus cibarius</i>	0.07	0.17	0.23; 6.23	0.05; 0.17
<i>Sarcodon imbricatus</i>	—	0.18	3.06; 0.36	1.87; 1.66

^a As compiled by Kabata-Pendias and Pendias,¹³⁵³ unless otherwise indicated.

^b Two values given for mushrooms of two different forest ecosystems.

^c Range of mean values (Falandysz et al., 2003).

and in the forms of organic compounds such as SeGSH (selenogluthathione), SeMet (selenomethionine), (DMSe) dimethylselenide and (DMdSe) dimethydiselenide, as well as protein-bound SeMet (Terry et al., 2000). Haygarth¹³²⁵ calculated that the absorption of Se by plants from atmospheric deposition contributes 33–82% of its total amounts in plants.

The kind of Se compounds added to soil (contamination or supplementation), as well as several plant factors, highly influences its species and absorption by plants. According to Terry and Zayed,¹⁵¹⁵ several metabolic processes are involved in the Se biomethylation; they emphasized the role of rhizosphere microbes. The Se phytovolatilization by broccoli is much higher from roots than from shoots, and higher for the SeMet than for inorganic Se compounds. Also, fungus and bacteria produce volatile DMSe (Frankengerger and Engberg¹³⁰³). Zayed and Terry¹⁵⁷¹ described the Se volatilization from roots and shoots under the impact of sulfate compounds.

Since Se and S share very similar properties, the Se compounds are absorbed and metabolized by mechanisms similar to those for S analogs (Terry et al., 2000). According to these authors, all soluble Se forms are likely to be taken up by plants; selenates and organic Se are driven metabolically; the uptake of selenites may have a passive mechanism. In general, organic Se are more readily available to plants than inorganic forms. Selenates, on the other hand, are likely to be easily transported to above-ground parts than selenites or some organic species (e.g., SeMet). Also selenates are more effective in increasing the S assimilation by lettuce than selenites (Rios et al., 2008).

The Se uptake by roots is controlled by several plant factors as well as soil and climatic conditions. Temperature is especially known to affect the Se uptake by plants with much higher rate at temperatures >20°C than during cooler seasons at temperatures <15°C. Rainfall may also highly influence the Se concentration of herbage. As Reuter⁶⁴⁹ reported that a low Se content in plants frequently occurs in high-rainfall areas.

Among soil factors, the pH seems to be most important and promotes higher Se availability (Figure 21.4). The role of rhizobium bacteria is significant in the Se uptake by plants. In some specific root–soil surface interactions, root exudates reveal a great ability to oxidize SeO₃ to SeO₄, which stimulates the availability of Se for plant uptake.¹²³⁰ Plants inoculated with bacteria have a fourfold higher rate of Se volatilization than noninoculated plants, which is probably due to the microbial increase in the Se uptake. The role of rhizobium bacteria is also significant in Se uptake by plants, for example, the inoculated plants have a fourfold higher rate of Se volatilization than the noninoculated plants, which is probably due to the microbially induced increase in Se uptake.¹⁵¹⁵ Interactions among S, Se, and O-acetylserine at the root–soil surface can also control the Se phytoavailability (Terry et al.¹⁵¹⁵).

2 Biochemical Functions

The Se function in plants has been investigated in many studies and there is still little evidence that Se is essential for all plants (Combs and Combs⁹⁶⁹). However, according to Terry et al. (2000), Se may be required for the growth of algae, but its essentiality to higher plants is controversial and yet unresolved. Recent studies on some grasses and vegetables provide indications that at a proper Se addition, the growth rate of these plants may be enhanced (Hartikainen, 2005; Turakainen et al., 2004; Xue and Hartikainen, 2000). Some data have indicated that this element may be required for Se-accumulating plants.⁵⁵⁵ Several compounds of Se, mainly with cysteine and methionine, were found in such plants (e.g., *Astragalus* species), but their metabolic functions have not been conclusively established. The Se-accumulator plants synthesize Se-methyl-cysteine, whereas nonaccumulator species produce Se-methyl-methionine. The physiological significance of this difference is not yet understood.¹³⁰³ A great proportion of the Se species in mushrooms is reported to be associated with low-molecular-weight components.¹¹¹⁹

Pyrzyńska (1995) cited that there are several naturally occurring Se species: (1) selenocysteine, (2) methylselenocysteine, (3) selenomethionine, (4) selenotaurine, (5) selenobetaine, (6) selenocholeline, (7) dimethylselenine, (8) dimethydiselenide, and (9) trimethylselenium. Although the essentiality of selenoproteins in higher plants has not been documented, syntheses of selenoproteins in

some plants (e.g., sugar beet) were reported (Terry et al., 2000). Several selenoamino acids, SeMet (selenomethionine), SeCys (selenocysteine), and SeMSC (Se-methylselenocysteine) in association with glutathione peroxidases were found in both bacteria and higher plants. Predominated forms of Se in plants, as reported by Djuić et al. (2001), are SeMet in cereal grains and legumes seeds, and SeMSC in vegetables. In lentils, the highest proportion (up to 95% of total Se) is present as SeMet (Thavarajah et al., 2007). In plants grown in soils with selenate addition, this Se species dominated; however, SeMet also was present at the concentration of 23% and 45% of the total Se content, in fodder radish and Indian mustard, respectively (Simon et al., 2007). The Se taken up by plants (ryegrass and lettuce) from Se-amended soil is incorporated mainly (up to 75%) in insoluble proteins. The activity of glutathione peroxide increases in plants with increasing Se doses, while superoxide dismutase activity and the concentration of vitamin E decrease.¹³²³ Lobanov et al. (2007) discussed the metabolism of Se-proteins in eukaryotes and concluded that aquatic organisms support the Se utilization whereas terrestrial ones reduce its uses.

Species and functions of Se in plants (mainly *Cruciferae*) were broadly discussed in several publications (LeDuc et al., 2004; Finley et al., 2005). Lyi et al. (2005) reported that the key factor responsible for the SeMSC formation (the most effective anticarcinogenic Se compound) is the SMT enzyme. Lyi et al. (2007) also observed that metabolism of S and Se in broccoli is controlled by the same enzymes. Apparently, this similarity occurs in other plants.

An antagonistic interaction of Se–Hg was reported for several plants. According to Khan and Wang (2009), Hg–Se compounds are responsible for these reactions which that a key role in alleviating the toxicity of both elements. The amount of Se absorbed by soybean roots increased in plants exposed to Hg (Yathavakilla and Caruso, 2007).

Results of recent investigations suggest that Se is an antioxidant that activates protective mechanisms, which alleviate oxidative stress in the chloroplasts and protect plants against UV induced stress (Xue and Hartikainen, 2000; Seppänen et al., 2003). Positive effects of Se on carbohydrate metabolism in some plants (e.g., potatoes, lettuce) were also reported by Turakainen et al. (2004). According to Djuić et al. (2004) the Se supplementation to plants (wheat and soybean) increases the tolerance to oxidative stress and improves mineral nutrient balance and vitamin E level. These authors concluded that under the Se supplementation, cereals and forage crops convert Se mainly into SeMet and incorporate it into proteins, although SeMet is not required for the growth of these plants. This form of Se dominates in most plants, and in wheat and soybean grown in Se-rich soils, 80% of the total Se consists of SeMet.

The toxic Se concentrations of nonaccumulator plants, resulting in a 10% reduction of yield, without visible symptoms, range from Se contents of 2–330 mg/kg in rice and white clover, respectively. In accumulator plants, Se concentration may reach 4000 mg/kg, without negative effects. Tolerance mechanisms involve processes of exclusion of active Se amino acids, thus preventing their incorporation into proteins and damaging effects on plant functions (Terry et al., 2000). The exclusion of Se from proteins in accumulator plants is the basis for their tolerance to Se. Generally, food crops have a low Se tolerance; however, most other plants may accumulate amounts of Se that are toxic to humans and animals.

In nontolerant plant species, an excess of Se may impair germination and growth, and cause chlorosis and black spots on leaves. Increased Se levels in plants suppress their concentrations of N, P, and S, as well as several amino acids. High Se concentrations inhibit the absorption of metals, mainly Mn, Zn, Cu, and Cd. These relationships are dependent on the ratio between the elements, and therefore stimulating effects of high Se levels on uptake of some trace metals may sometimes be expected. The application of N, P, and S is known to help in detoxifying Se, which may be a result either of depressing the Se uptake by roots or of establishing a beneficial ratio of Se to these elements.

3 Concentration in Plants

There is a positive linear correlation between the Se in plant tissues and the Se content of soils, and Sippola⁷³⁴ stated that the total soil Se gives a better measure of plant response than do its soluble

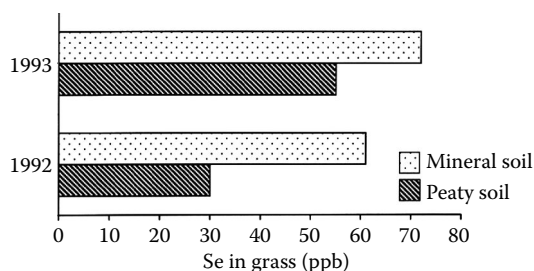


FIGURE 21.5 Se content in grass (an average of 10 grass species) grown in two soils: (a) mineral, pH 6.5, OM 1.2%, Se 0.07 mg/kg, and (b) peat, pH 5.5, OM 75%, Se 0.71 mg/kg. (Reproduced from Borowska. K. and Lyszcza, R., The selenium concentration in some grass species from mineral and peaty soils, *Proc. 16th General Meeting of the European Grassland Federation*, Grado, Italy, September 15–19, 707, 1996. With permission.)

fractions, which contrasts with other opinions.⁹⁶⁹ Johnson et al. (2000) concluded that Se-grain status is the best means of defining its phytoavailability in soils.

The complex impact of variable factors on the Se uptake by plants can significantly alter the relation of Se in plants and soils. As presented in Figure 21.5, grass can take up more Se from mineral soil with 0.07 mg Se/kg than from peat soil with 0.71 mg Se/kg. A significant variation in Se contents of wild plants was observed, regardless of its concentrations in soils. Miladovic et al.¹⁴¹⁹ found considerably higher contents of Se in hairy milk-vetch (155–177 µg/kg) than in comfrey (62–118 µg/kg), growing in the same site, but varied within the stages of plant growth. Most plants contain rather low Se, around 25 µg/kg and rarely exceed 100 µg/kg. However, some plants reveal a great capability to accumulate Se and they may concentrate Se to extremely high levels (over 1000 mg/kg).

TABLE 21.7
Selenium in Food Plants from the United States^a
(µg/kg FW)

Plant	Range ^b	Average
Carrot	6–29	17
Potatoes	4–23	13
Cauliflower	0–100	9
Tomato	0–19	2
Onion, bulb	0–39	6
Green beans	0–13	1
Apple	3–6	4
Orange	0–12	1
Strawberries	0–12	3
Brazil nuts	200–253,000	14,700
Brazil nuts ^c	70,710–87,320	—
Coconut ^c	405–678	—

^a Adapted from ATSDR (2002).

^b Due to a lack of the detection limit, the minimum value is given as 0 (zero).

^c Brazil coconut, defatted base, after Kápolna et al. (2004).

TABLE 21.8
Selenium in Wheat Grains from Different Countries^a (μg/kg)

Country	Range	Average
Algeria	910–1040	920
Australia (Queensland)	1–117 (<50–>200) ^b	23
Canada (barley)	9–38	21
Czech Republic	11–49	25
Denmark	4–87	21
Egypt	140–430	340
Finland ^c	10–70	—
Finland ^d	76–190	142
France	30–53	36
Norway	1–169	33
Poland	—	42
Sweden ^e	2–71	14
U.S.	280–690	490
Yugoslavia	<10–25	—
China (maize-corn) ^f	2–198	—

^a From various sources as compiled by Kabata-Pendias and Pendias,¹³⁵⁷ unless otherwise indicated.

^b Data for Queensland, after Oldfield (2002).

^c Data before the Se supplementation program (Fordyce, 2005).

^d Data for spring wheat in the period 1998–2001 (Eurola et al., 2003).

^e After Eriksson (2001).

^f Geometric mean values, for low and high Se soils, respectively, after Fordyce et al. (2000).

The Se content of crops received recently much attention because of its importance in the food chain. Thus, most data that are available are for food and fodder plants (Table 21.7). Especially, cereal grains, as the most common source of Se in diets, have been broadly analyzed (Table 21.8). In general, mean concentrations of Se in grains are higher in countries from arid climates than in countries from humid climates. Finland is an exception, having implemented the program of Se addition to fertilizers. According to Govasmark and Salbu (2009) the bioaccessibility of Se in Se-enriched wheat is higher from the flour than the bran, but since Se contents are higher in bran, the nutritional Se-efficiency is equal.

Fordyce (2005) presented (after Jacobs) variation in average Se contents of various crop types of the United States, as follows (in μg/kg): (1) 407, roots and bulbs; (2) 297, grains; (3) 110, leafy vegetables; (4) 66 seed vegetables; (5) 54 vegetable fruits; and (6) 15, tree fruits.

The common range of mean Se levels varies from 340 to 920 μg/kg for countries with high Se levels in grains, and from 14 to 42 μg/kg for countries with low Se levels in grains (Table 21.8). These variations do not indicate a significant impact of climatic conditions, because several other factors also control the Se absorption by plants. According to Farnham et al. (2007) environmental effect on the Se concentration in broccoli was about 10 times larger than genotype impact. A variation in the Se uptake by various species of the same plant (*Astragalus*) is described by Somer and Caliskan (2007).

In areas with low soil Se, applications of sodium selenite to soils or as a foliage spray are proposed for correcting Se nutritional deficiencies. In view of the toxic properties of Se salts; however, these practices should be carefully controlled. The addition of Se to soil (at 10 g/ha) affected its contents in grains of barley and oats, from 19 to 260 μg/kg and from 32 to 440 μg/kg, respectively

TABLE 21.9
Selenium in Food Plants from Areas of Different Se Levels in
Soils of China^a (µg/kg)

Plant	Se Levels of Soils		
	Low	Moderate	High
Corn, grains	—	50	6900
Sweet corn	0.5–3	75–85	2800
Wheat, whole grains	6	40	1100
Cabbage	—	2–38	2900
Potatoes	2	6	400

^a After Combs and Combs.⁹⁶⁹

(Gupta and Gupta, 2000). Foliar application of Se on potatoes resulted in its increased level in tubers, from 0.465 mg/kg in control up to 1068 mg/kg in experimental plants (Hlušek et al., 2006). Ducsay et al. (2006) observed an increase of Se contents of winter wheat grains after the Se foliar application (Se doses 10 and 20 g/ha) from 0.094 to 0.192 mg/kg and concluded that the Se dose 10 g/ha is sufficient for reaching the required Se content in wheat grains.

Enriched Se content of garlic has often been reported as an important dietary supplement (Maksymovic,¹³⁹⁵ Ip et al., 2000). Commonly observed increased levels of Se in Brazil nuts (*Bertholletia excelsa*) may highly vary, depending on the growth conditions (Table 21.7). For instance, nuts that were grown in soils derived from Cretaceous sediments enriched with Se by volcano emissions contain more Se than those grown in lower Se soils.

Mean Se contents in some food plants in Finland, after the Se supplementation program, varied in the period from 1989 to 2001 (in µg/kg) as follows: (1) potatoes, 31 and 110; (2) carrots, 20 and 40; (3) white cabbage, 160 and 580; and (4) strawberries, 10 and 11 (Eurola et al., 2003; Eurola, 2005). All food plants grown in seleniferous or Se-contaminated soils contain much more Se than plants grown in low Se soils (Table 21.9). Ge and Yang (1993) analyzed a number of feed and forage samples from China and found that samples from the Se-deficient regions contain this element at the following levels (in µg/kg): (1) <20, severe deficient areas; (2) 30–50, deficient areas; (3) 60–90, moderate deficiency areas; and (4) >100, adequate Se supply areas.

The Se content of forage plants has also been of a great concern. Leguminous plants (clover and alfalfa) contain usually more Se than grasses (Table 21.10). The highest Se averages of leguminous plants are reported for India and the United States, 672 and 320 µg/kg, respectively, while for other countries it varies from 15 (Canada) to 90 µg/kg (Germany). Average values of Se in grasses vary from 13 (in Canada) to 352 µg/kg (in India); however, it is difficult to observe any regular variation. As cited by Oldfield (2002), some times a grass (*Agrostis tenuis*) may accumulate 2–7 times as much Se as white clover (*Trifolium repens*).

II TELLURIUM

A INTRODUCTION

The average content of tellurium in the Earth's crust is estimated as 0.005 mg/kg (Table 3.2). Its abundance in rocks varies from 0.001 to about 0.01 mg/kg, with a tendency to elevated concentrations in argillaceous rocks (Table 21.2). Increased Te levels in coal and fly ash (0.02–2 mg/kg) reveal an affinity to be sorbed by OM (Llorens et al., 2000). Volcanic gases and volcanic sulfur deposits are usually enriched with this element. Te resembles Se and S in a number of properties, but is more

TABLE 21.10
Selenium in Forage Plants from Different Countries^a (µg/kg)

Country	Grass		Clover or Alfalfa	
	Range	Average	Range	Average
Canada	8–23	13	5–31	15
Czech Republic	75–85 ^b	—	—	—
Denmark	—	32	—	35
Germany	30–210	110	5–130	90
Finland ^c	120–240	—	—	—
France	19–134	47	36–39	38
India	200–450	352	440–870	672
Japan	5–174	43	6–287	33
Sweden	11–64	30	18–40	—
U.S.	10–40	32	30–880	320

^a From various sources as compiled by Kabata-Pendias and Pendias,¹³⁵⁷ unless otherwise indicated.

^b Range of mean values (Wagner et al., 2004).

^c Range of mean contents in silage, after the Se supplementation program (Eurola et al., 2003).

metallic in nature than either of these elements. Te shows variable valences from –2 to +6 and easily forms di- and trivalent oxides (Table 21.1).

The most common Te minerals are: tellurite, TeO_2 ; sylvanite, $(\text{Ag}, \text{Au})\text{Te}_4$; hessite, Ag_2Te ; calaverite, AuTe_2 ; tetradyomite, $\text{Bi}_2\text{Te}_2\text{S}$; krennelite $(\text{Au}, \text{Ag})\text{Te}_2$; and nagayagite, $\text{Au}(\text{Pb}, \text{Sb}, \text{Fe})_3(\text{TeS})_{11}$. Minerals of Te are commonly found in pyritic ores, and in Au and Ag tellurite deposits. During weathering, Te is oxidized to slightly mobile tellurite that is readily sorbed by Fe hydroxides. Its migration in hipergenic zones is rather limited; however, its complex anion, TeO_3H^- , is easily mobile.

The global Te production in 2008 was estimated as 38 t, only for Canada and Peru (USDI, 2009). According to Kobayashi (2004), its global production in 1999 was about 124 t. Tellurium is mainly a by-product of Cu smelting and/or electric refining of Cu. Also, refining of other metals, for example, Pb, may be a source of Te.

Compounds of Te are used to improve properties of metal alloys and stainless steel. It is added as vulcanizing agent for rubbers to increase resistant to heat and abrasion. Due to relatively great conductivity, Te is used in semiconductors and other electronic devices. It is also a catalyst and in vapor form, it is applied in “daylight lamps.” It is used in some ceramics. Photographic and pharmaceutical industries also utilize some quantities of this element.

B SOILS

There are scarce data on Te contents of soils. Mean values for soils are given as 0.006 mg/kg (Reimann and Caritat 1998) and 0.03 mg/kg (FOREGS, 2005). Average Te level in soils of the United States is estimated as 0.04 mg/kg (Burt et al., 2003).

In reference soil of China, Te contents vary from 0.03 to 4.0 mg/kg and in soils of the United States, the range is between 0.02 and 0.69 mg/kg (Govindaraju¹³¹³). Hashimoto et al. (*vide* Kobayashi, 2004) reported mean soil Te to be 0.035 and 0.031 mg/kg in Japan and Korea, respectively. Asami et al.¹²⁰⁷ found elevated concentration of Te in soils in the vicinity of nonferrous metal smelters. Geometric mean values for Te in soils surrounding various smelters range from 0.1 to 0.5 mg/kg, but the maximum value was reported to be 6.55 mg/kg. Soils of mining districts in the United States (the state of Nevada) contain a high concentration of Te up to 10 mg/kg (Cowgill, 1988).

Te-rich soils are in the vicinities of Au mineralization. Schroeder et al.⁶⁹⁷ also reported a relatively high concentration of Te in various soils, up to 37 mg/kg.

Tellurium distribution in soils may suggest some biomagnification in upper soil horizons when compared with its range found in various rocks. Since the biological cycling of Te resembles that of Se, the microbial metabolism of Te also seems to be similar to that of Se. Thus, bacteria capable of methylating Se and As can also methylate Te, whereas the reduction of tellurite to elemental Te can readily occur under the influence of variety of microorganisms. Weinberg⁸⁵⁶ stated that bacteria capable of methylating As and Se can also methylate Te, whereas the reduction of tellurite to Te can readily occur under the influence of a variety of microorganisms. Both biological and/or abiological methylation of Te increases its mobility. Tellurite reductase was identified in some bacteria and the reduction of selenate and tellurite by nitrate reductases was reported (Sabaty et al., 2001).

According to Harada and Takashi (2008), Te is mainly associated with Fe³⁺ hydroxides under oxic conditions, but is also likely to be scavenged by Mn oxyhydroxides. Under reducing conditions, a stepwise change from Te⁶⁺ to Te⁰ via Te⁴⁺ occurs.

C PLANTS

Vegetables contain Te within the range of <0.013–>0.35 mg/kg FW, being the lowest in apple fruits and the highest in onion and garlic, up to about 300 mg/kg.^{574,697} The garlic odor of some plants is caused by vapors of dimethyl tellurite. The mean Te content of cereal grains from Sweden is <0.001 mg/kg (Eriksson, 2001). Norwegian mosses sampled in the period 1990–1995 contained Te at average value of 0.005 mg/kg (Berg and Steinnes¹²²³).

Plants take up Te, similarly as Se, relatively easily and when its content in growth media is high, there is a corresponding increase in the Te content of plants. Seleniferous plant species (e.g., *Astragalus*) also contain elevated quantities of Te (up to 6 mg/kg), particularly when grown in a Te-enriched soil. In vegetation growing in some mining districts, for example, copper mine in Nevada, increased level of Te, up to 1 mg/kg, was observed. Its highest accumulation was in flowers (Cowgill, 1988). Bowen⁹⁴ cited high Te accumulation, from 2 to 25 mg/kg, in a few plants from Te-rich soils. Schroeder et al.⁶⁹⁷ also reported a relatively high concentration of Te in plants, within the range of 0.7–6 mg/kg.

III POLONIUM

A INTRODUCTION

Abundance of Po in the Earth's crust is in the order of 1 fg/kg (10⁻¹⁵ %). However, other sources estimated its possible occurrence in the bulk continental crust as 2 pg/kg (10⁻¹² %). Some accumulation may be expected in coal. Uranium ores contain Po up to about 0.1 µg/kg and are the main source of this radionuclide. Increased Po concentration is in P rocks, possible due to its capture during the formation of rocks.

There are 25 known isotopes of Po with atomic masses ranging from 194 to 218 (Table 21.1). Seven Po isotopes occur naturally. The only one occurring to any extent is ²¹⁰Po, with the half-life of 138.4 days. This radioactive isotope is relatively ubiquitous in the environment but tends to be elevated in uraninite/pitchblende (at approximate concentration 10 ng/kg) and in phosphate-related materials. It is also associated with various uranium and thorium minerals, and with the radioactive decay within uranium chains U–Ra–Pb. The precursor nuclides of ²¹⁰Po are ²²²Ra and ²¹⁰Pb. Po is chemically similar to Te and Bi and possibly may follow the biochemical pathway of Se and Te.

Uses of ²¹⁰Po are in nuclear batteries, neutron sources, and film cleaners. It is also used as light-weight heat source for thermoelectric power in space satellites.

While using Po compounds a great control is needed to minimize health hazards to users.

B SOILS

The natural abundance of ^{210}Po in soils is reported to range from 10 to 220 Bq/kg. This is the result of ^{222}Rn decay in the top layer of soils and atmospheric fallout of the ^{210}Po suspended in the air. This radionuclide is fixed almost irreversibly to particles of soil, mainly by metal hydroxides and/or sulfides. It is not a very mobile element and is likely to be bound by SOM. A close correlation between the soil levels of ^{210}Po and SOM contents (Korenkov et al., 2000) was observed. These authors reported the ^{210}Po levels in soils of Moscow to be at the range of 30–50 Bq/kg. There are some suggestions that Po can be methylated, similar to the way in which Hg, Se, and Te are methylated.

The mean activity of ^{210}Po in soils of the U-ore area in India is 124.8 Bq/kg (Marbaniang et al., 2009). Significantly higher concentrations (15,000–22,000 Bq/kg) can be found in various uranium mine tailings. Areas of phosphate ore processing and waste disposal are also enriched with this radionuclide. Arthur and Markhan (1984) reported that concentrations of ^{210}Po in soils and wild animals (deer and mice) collected near radioactive waste disposal in the vicinity of the phosphate processing plant in the Idaho State, United States, were about three times greater than from the other sampling locations.

C PLANTS

The natural abundance of ^{210}Po in terrestrial plants ranges from 8 to 12 Bq/kg.⁹⁴ Elevated contents of this radionuclide in some vegetables and tobacco plants can be derived from either the soil or the air and apparently reflect pollution with radionuclides.^{549,710} According to Marbaniang et al. (2009), the ^{210}Po activity in plants from the area of U-deposit in India varies from 0.02 to 9.69 Bq/kg. Increased contents of this radionuclide is observed in plants, and especially in tobacco, grown in soil heavily fertilized with some phosphate-based materials. Increased level of this radionuclide may also reflect an aerial source of pollution. However, the stage of leaf development and the methods used to cure leaves affected the final amount of ^{210}Po in tobacco leaf. The ^{210}Po concentration of tobacco leaves is of great health concern, not only to smokers. Khater and Al-Sewaidan (2006) reported that the activity concentration of ^{210}Po in cigarette tobacco was 15.1 (5.5–22.2) mBq/cigarette. Cigarettes produced in Poland contained 4.23–24.12 mBq/cigarette (Skwarzec et al., 2001).

Relatively widespread use of radioactive phosphate fertilizers may increase levels of radioactive Po in food and feeds. However, it is not clear yet how much radioactive content fertilizers contribute to the ^{210}Po activity of plants and how much it is naturally present. Nevertheless P fertilizers, usually enriched with ^{210}Po , are considered to be the main source of this radionuclide in plants, and in tobacco leaves, in particular. Relatively greater ^{210}Po contents in tobacco leaves resulted from P-fertilizers than in other plants is apparently associated with a large leaf surface, which suggests that the main Po source is from the atmosphere deposition. As a very volatile element, Po is likely to be also absorbed by broad-leaved vegetables.

Mushrooms are known to be good bioindicators for some elements from aerial deposition. Thus, elevated content of ^{210}Po in mushrooms, and in the high King Bolete (*Boletus edulis*), in particular, indicates its aerial source. As Skwarzec and Jakusik (2003) reported, the ^{210}Po concentration is higher in *Boletus edulis* than in other wild mushrooms, within the range of 20.10–76.47 and 9.89–47.93 Bq/kg, in caps and stipes, respectively.

The variable ^{210}Po concentrations in phytobenthos species within the range between 0.12 and 1.12 Bq/kg indicate the impact of several factors on its bioaccumulation. As Skwarzec et al. (2003) estimated, the BCF value of phytobentos for this radionuclide is high and vary from 450 to 4400.

According to Skwarzec and Prucnal (2007), the activity of ^{210}Po in herbivorous animals (deer *carvidae*) from northern Poland is at the background level; the average values range from 0.02 to 7.15 Bq/kg, in muscles and kidneys, respectively.

22 Elements of group 17 (Previously Group VIIa)

The 17th group of the Periodic Table is composed of three trace elements: fluorine (F), bromine (Br), and iodine (I). To this group of elements belongs chlorine (Cl), which is relatively common in the biosphere, but some authors have treated it as a trace element. I is the least reactive of the elements in this group. The last element of this group, astatine (At), occurs as radioactive unstable isotopes of very short lives (the longest half-life of ^{209}At is 8.1 h).

Elements of this group, called halogens, are nonmetals and in nature form simple anions, commonly at the -1 oxidation stage (Table 22.1). With an exception of F, halogens reveal an affinity to combine with oxygen and play a significant role in several biochemical processes. These anions are highly mobile in the Earth's crust.

I FLUORINE

A INTRODUCTION

The average content of F in the Earth's crust is estimated as 625 mg/kg (Table 3.2).

It is slightly concentrated in mafic rocks, up to 1200 mg/kg, when compared with its content in acid igneous rocks (<850 mg/kg) and to its abundance in sedimentary rocks (<800 mg/kg) (Table 22.2). It is likely to be concentrated in argillaceous sediments and in black shales. High levels of F are known to be associated with some phosphate deposits, over large areas of some continents (e.g., Africa, America). A strong association of F with phosphates is observed in both primary and secondary minerals. Fe concentrations in fluorite forms also occur in some dolomites as fissure veins and other forms. Compounds of F are common constituents of magmatic and volcanic exhalations, and sometimes may occur in rocks as gaseous nebulae.

Fluorine is a very reactive element (most of the halogen group) and may combine with several other elements, including inert gases. Its most common mineral, fluorite (as a salt, it is called as fluoride and fluorspar), CaF_2 , is widely distributed in both lithosphere and hydrosphere. Sellaite, MgF_2 , is often associated with fluorite. Other commonly exploited minerals are cryolite, $\text{Na}_3(\text{AlF}_6)$; and fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Topaz, $\text{Al}_2\text{F}_2\text{SiO}_4$, is a popular gemstone. Several minerals, like micas and amphiboles, may be associated with fluorapatite. In hypergenic zones, cryolite is most readily soluble, and mobile F is easily sorbed by clay minerals and phosphorites.

Fluorite is the most common commercial source of F. World total, excluding the United States, production of fluorite was estimated for 2008 as about 5840 kt (USDI, 2009).

A great proportion of F goes to the aluminum industry. In the steel industry, it is applied as hydrofluoric acid. It is also used in plastic, ceramic, and glass production. Being a highly oxidizing agent and exothermic in chemical reactions, F is broadly used in various chemical processes. It is a common compound of freon gases, chlorofluorocarbons (CFCs), used for the refrigeration. Perfluorooctane sulfonate (PFOS), very persistent chemical, is applied as stain repellent.

Fluoride has long been added to municipal drinking water (at the level of 1.2–1.9 mg/L) for the prevention of tooth decay. It is still added to toothpastes.

TABLE 22.1
Selected Properties of Trace Elements of Group 17

Element	Atomic Number	Atomic Mass	Atomic radius ^a (pm)	Density (20°C) (g/cm ³)	Valence ^b
F, fluorine	9	18.99	57	1.69 ^d	-1 (+1 to +7) ^e
Cl, chlorine	17	35.42	97	3.21 ^d	-1 (+1 to +7) ^e
Br, bromine	35	79.90	122	7.59 ^d	-1 (+1 to +7) ^e
I, iodine	53	126.90	132	4.93	-1 (+1 to +7) ^e
At, astatine	85	[210] ^c	143	—	-1 +3, +5

^a Approximately average values for the main oxidation states.

^b Valence value in bold are for the main oxidation states.

^c Variable atomic mass of unstable isotopes from 196 to 219.

^d Density in g/L (gases).

^e Range of other oxidation states.

B SOILS

The average F contents of worldwide soils have been calculated to be 321 mg/kg (Table 3.2). The common contents for most soils seem to range from 150 to 400 mg/kg.¹³⁵⁷ The F content of soils is inherited from parent material, but its distribution reflects soil-forming processes and soil texture. Relatively close positive relationship between F and clay fraction contents is evident. The lowest F amounts are in Arenosols, Podzols, and Histosols, and the highest contents occur in Cambisols (Table 22.2). Very high levels of F, above 1000 mg/kg, are reported for uncontaminated soils derived from F-rich bedrocks that are associated with the provinces of endemic fluorosis (Fuge and Adreus,¹⁰⁰¹ Ermakov, 2004). A great increase of F (up to 40.8 mg/L) in groundwater of such areas is of a great environmental concern (Chae et al., 2007).

TABLE 22.2
Abundance of Trace Elements of Group 17

Rock/Soil	F	Cl	Br	I
Earth's crust	625	640	2	0.5
Igneous rocks	—	—	—	—
Mafic	300–1200	40–300	0.2–3.0	0.007–0.5
Acid	300–850	130–300	0.2–4.5	0.01–0.5
Sedimentary rocks	—	—	—	—
Argillaceous	500–800	100–200	5–10	1–38
Sandstones	50–270	10–20	1–5	0.02–1.5
Calcareous	50–350	50–350	<1–6	0.5–3.0
Soils ^a	321 ^b	300 ^b	10 ^b	2.8 ^b
Arenosols (sandy)	80–205	115	<1–8	<0.1–10
Podzols (medium loamy)	175–462	—	7.9–8.2	0.3–10
Cambisols (heavy loamy)	470–1360	1000	50–104 ^c	50–104 ^c
Calcisols (calcareous)	470–680	—	68–130 ^c	0.3–10
Histosols (organic)	<0.1–350	—	—	1–10

^a Soil groups are given according to the WBR (Table 3.1).

^b World-soil data (Table 3.2).

^c The highest values are for volcanic ash soil.

The behavior of F in soils is controlled by several soil parameters, mainly by clay contents, pH, and concentrations of Ca and P. Soil can accumulate relatively high amounts of F, particularly in B horizons, which usually are enriched with amorphous Al-oxides/hydroxides.

Under natural soil condition, F is slightly mobile; however, in acid soils its solubility usually increases due to the occurrence of readily soluble fluorides such as NaF, KF, and NH_4F , whereas AlF_3 , CaF_2 , and MgF_2 are known to be of a low solubility. The F mobility in soils is variable and highly controlled by pH, its higher solubility is at pH below 5 and above 6. In soil solution, F occurs mainly as complex cations: AlF_2^+ and AlF_2^+ , as well as anions: F^- and AlF_4^- . Also, other ion pairs may occur: AlF_6^{3-} , SiF_6^{2-} , and BF_4^- (Kabata-Pendias and Sadurski, 2004). The mobile F^- in the soil solution might control the activity of Al^{3+} (Lindsay⁴⁷⁷).

The most common forms of F in soils is fluorapatite; however, several fluorides (e.g., AlF_3 , CaF_2) and aluminosilicates [e.g., $\text{Al}_2(\text{SiF}_6)_2$] are also reported to occur in soils. In calcareous soils, the occurrence of slightly soluble fluorides and complexes with Fe, Al, and Si are responsible for a low migration of this element. In sodic soil, on the other hand, a high level of exchangeable Na affects increased solubility of F. The sorption of F by acid soils is attributed to interactions with Al oxy/hydroxy species.¹¹¹⁸ As F is known to readily replace hydroxyls of clays, the clay minerals, illites in particular, are believed to be the seat of most of this element in soils. The range of F content of illite and chlorite mineral groups is reported as 0.1–2.3% (Thomas et al.⁷⁸¹).

The F behavior in soils was studied by Larsen and Widdowson,⁴⁶¹ Perrott et al.,⁶⁰⁷ Chhabra et al.,¹³⁷ and Omuetti and Jones.⁵⁸⁴ The obtained results show that the mobility of F in soils is complex and that the predominant factors controlling the level of this ion in soil solution are the following soil parameters: clay minerals, pH, and concentrations of Ca and P. In general, the greatest adsorption of F by soil mineral components is either at the distinct acid range of pH, or at about pH 6–7 (Figure 22.1). In calcareous soils, the formation of slightly soluble CaF_2 and F complexes with Fe, Al, and Si are responsible for a low migration of this element. In sodic soils, on the other hand, a high exchangeable Na affects increased F solubility. Under natural soil conditions, F is slightly mobile, but it is not accumulated in the surface horizon, especially of acid soils. The high solubility of F in acid soils is attributed to the occurrence of readily soluble fluorides such as NaF, KF, and

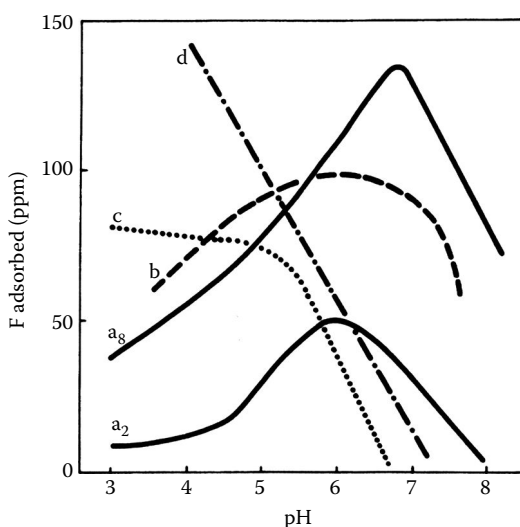


FIGURE 22.1 Adsorption of F by soil and clay as a function of pH. Soil (a_2 and a_8) equilibrated against 2 and 8 mg F^- per liter solution, respectively. All clays: (b) bentonite; (c) bauxite; and (d) kaolinite, equilibrated against 2 mg F^- per liter solution. (From Omuetti, J. A. I. and Jones, R. L., *J. Soil Sci.*, 28, 564, 1977. With permission.)

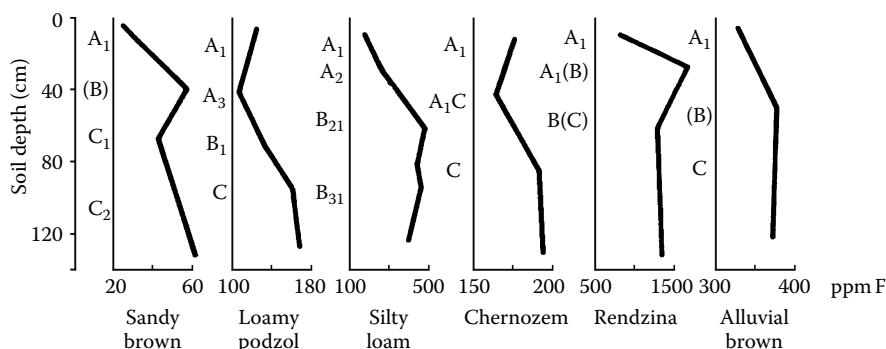


FIGURE 22.2 Distribution of F in the profiles of different soils developed under humid climate. (Letters indicate genetic soil horizons.)

NH₄F, whereas AlF₃ is known to be of a low solubility. Thus, the increasing F content with depth reflects the response to the soil pH; however, the enriched clay content usually contributes more to the F distribution in soil profiles. This relationship with clay content was reported by Piotrowska and Wiacek.⁶¹⁹ Apparently, F is lost from the surface horizons of the most soils (Figure 22.2) and this reflects partly a low F affinity for OM. Omueti and Jones⁵⁸⁴ gave the range in F concentrations in SOM of surface horizons to be as low as 0.03–0.12 mg/kg. However, in some tropical soils, organically bound F (monofluorinated compounds) may occur and affect its high availability to plants. The origin of these F compounds might be attributed to the synthesis by certain microorganisms.¹³⁵⁷

Soil pollution by F became, in some regions, ecologically important. Several sources, but mainly Al smelters and P fertilizers factories, are still significant emitters of F to the atmosphere. Soils surrounding Al-processing industries, china clay industries, and P-fertilizer factories are reported to contain F above 3000 (Table 22.3). The highest F content, within the range of 620–19,960 mg/kg was reported for soil surrounding old mining regions in the United Kingdom.¹⁰⁰¹

Artificially high soil F levels can also occur through contamination by the application of phosphate fertilizers, sewage sludge, and pesticides (Table 22.3). Natural fluorapatite might be utilized as phosphate fertilizer. Assuming a high F content of phosphate fertilizers (common range 8500–38,000 mg/kg), an input of F to arable soils may be of ecological importance. Wu et al. (2007) reported a market elevation in the F content of surface soils with increasing age of tea plantation.

Emissions of F from industrial sources are known to introduce soluble fluorides into the surface layer of soils. Fluorides moving down the soil profile extract those elements that form stable and/or

TABLE 22.3
Fluorine Contamination of Surface Soils (mg/kg)

Site and Pollution Source	Maximum or Range of Content	Country	Reference
Old mining area	2000	Great Britain	166
Al-processing industry	1350	Czech Republic	500
	1500–3200	Poland	85
Other metal-processing industry	305–345	Poland	512
China clay industry	1200–3560	Great Britain	1001
P fertilizer manufacturer or application	308–2080	Canada	478, 782
	385 ^a	Poland	620

^a After 10 years of P fertilizing, against the background value of 296 mg/kg F.

soluble fluoro-complexes. The F compounds added to soils by pollution are usually readily soluble and thus available to plants. Most of the added F to soil is either effectively fixed by soil components (clays, Ca, and P) or readily removed from light soils by water. More F is usually absorbed by acid soils than by alkaline ones. Easily soluble F-bearing fertilizers (e.g., potassium fluoroborate) or sewage sludge may affect a remarkable increase in the F bioaccumulation.^{166,857} Continued F deposition will affect its accumulation in surface soils and may increase the availability to plants and soil biota.

The most important hazard of F contamination in soils concerns changes in soil properties due to the great chemical activity of hydrofluoric acid, which is temporarily formed from both solid and gaseous F pollutants. Bolewski et al.⁸⁵ reported the decomposition of clays and other silica minerals in soil having heavy F pollution. They also reported the destruction of humic mineral complexes resulting in a significant loss of OM in soils. The reduction of enzymatic activity of some soil microorganisms with the addition of NaF was reported by Russel and Swiecicki.⁶⁷⁰ Findings of Grishko¹³¹⁸ indicated that soil microorganisms using organic nitrogen forms are more resistant to harmful effects of F pollution than bacteria using inorganic nitrogen compounds. The phytoavailability of F in polluted soils is a function of a number of soil characteristics and is not the only cause of limited plant growth in those soils.

Presently, a great attention is given to the possible formation of highly toxic organic F compounds that can be synthesized by both higher plants and microorganisms under various soil conditions.²⁸⁸ Although a high F level in soils is not itself harmful to plants, F-polluted soils should be ameliorated for a proper growth of vegetation. The application of materials that increase the sorption capacity or fixation ability for F ions is known to improve soil properties and to limit F uptake by plants. Effective amelioration of F-polluted soils is presently of a great environmental concern.

C PLANTS

1 Absorption and Transport

The availability of F to plants is usually not closely related to total or soluble F contents of a soil. However, under certain soil and plant conditions, the F content of plants seems to reflect its occurrence in soils.⁷²³ Bieliyakova⁷³ gave the ratio of F in plant ash to F in topsoils as 0.2 and 0.6 for cultivated and natural vegetation, respectively. These values indicate a relatively low F bioavailability. The F concentration in orange leaves, however, showed a fairly close relationship with hot-water-soluble F in soil.¹²¹⁰ The stimulating effect of increased levels of Cr⁶⁺ in soils on the F uptake by plants was observed, but the mechanism is not yet understood.¹⁵⁷⁴

The soluble F fraction in soil is taken up passively by roots and apparently is easily transported in plants. This statement is supported by the observation of a ready F uptake from fields irrigated with F-containing waters. Most often, the availability of F increases with decreasing soil pH. Vandeputte¹¹⁷⁶ found that F absorption from the solution media by alfalfa and wheat is positively correlated with F concentration. The author obtained results that indicated a very high F accumulation in cereal grains (up to 3250 mg/kg at 50 mg/kg F⁻ in solution). This phenomenon reflects a possible influence of the formation of an F complex that may be more easily taken up by plants than are F ions. Hall³⁰⁰ found that in particular tropical soils, organically bound F (monofluorinated compounds) may occur. These compounds are shown to be highly available to plants, and highly toxic to animals. Their origin, however, is not yet clear, but presumably they are synthesized by certain microorganisms.

Although it has been shown that plants can take up F quite easily from polluted soils, the bioavailability of soil F is of much less significance than that from airborne compounds. The effects of atmospheric F depositions, both in soils and on plant surfaces, were extensively studied. The results, as summarized by Groth²⁸⁸ and Weinstein,⁸⁵⁷ indicated that the deposition of airborne F on soil has little or no effect on the F content of plants. However, when F is present as both an air pollutant and a soil pollutant, the F uptake by plants from air is much more significant than their uptake from soil. Several factors affect plant accumulation of airborne F, but the most pronounced are atmospheric F concentration and the duration of exposure (Figure 22.3).

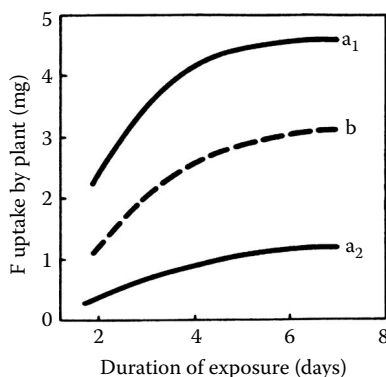


FIGURE 22.3 F uptake by plants as a function of the F contamination in air and of exposure time. Beans, tops (a₁ and a₂) at F concentration of 11 and 5 $\mu\text{g}/\text{m}^3$, respectively. Tomato plants (b) at F concentration of 5 $\mu\text{g}/\text{m}^3$. (Adapted from Kabata-Pendias, A. and Pendias, H., *Trace Elements in the Biological Environment*, Wyd. Geol., Warsaw, 300, 1979 (Po).)

Foliar uptake of gaseous F apparently follows the path of the penetration of other gases into the leaves. Chamel and Garbec¹²⁵ reported that F penetration through the cuticle is slight; however, under natural conditions, most leaf surfaces have open stomata and also show breaks and punctures that facilitate the F uptake by foliage. Soluble F compounds are also known to be absorbed through the cuticle when deposited on the leaf surface. When F is accumulated in vegetative tissues during exposures to gaseous HF, it is not translocated to the developing grains.⁴⁹⁹ Biological factors such as plant species, stage of development, and others are very important determinants of the F bioaccumulation.

2 Biochemical Functions

Centuries ago, symptoms of F toxicity to animals were observed after volcanic eruptions. During the last century, the role of plants as a sink for emitted F and its transfer to animals was recognized. Contemporary investigations on grasses collected immediately after the eruption of Hekla volcano in Iceland in 1970 showed that their F content was 4300 mg/kg, and that it rapidly decreased during 40 days to a concentration of less than 30 mg/kg.⁵⁹⁸

At present, F is considered to be the most hazardous and the most phytotoxic trace pollutant among the common air pollutants such as O₂, SO₂, and NO_x. The phytotoxicity of airborne F is influenced by ecological and biological factors and also by its physical and chemical characteristics. Effects of atmospheric F on plants were extensively reviewed by Groth,²⁸⁸ Kluczynski,⁴⁰¹ and Weinstein.⁸⁵⁷ There is no evidence of the F phytotoxicity when this element is absorbed by roots, whereas airborne F, especially when it occurs as hydrofluoric acid, is highly toxic. The most emphasized effects of F on plant metabolism are related to:

- Oxygen uptake decrease
- Respiratory disorder
- Assimilation decrease
- Reduction in chlorophyll content
- Inhibition of starch synthesis
- Inhibition of pyrophosphatase function
- Altered metabolism of cell organelles
- Injured cell membranes
- Disturbance of DNA and RNA
- Synthesis of fluoroacetate, a most hazardous F compound

Although Shkolnik⁷¹⁸ and Weinstein⁸⁵⁷ reviewed studies on plant growth stimulated by F, neither a plant requirement for this element nor its essential role in plant metabolism was established. As Weinstein⁸⁵⁷ described, the apparent stimulation of some isoenzymes (e.g., acid phosphatase and dehydrogenase) by HF fumigation may, in fact, be a result of the inhibition of other enzymes.

Interactions between F and other elements are not unanimously agreed upon. There is some evidence that an increased F content is likely to inhibit the absorption of several nutrients, whereas a synergistic effect, mainly to P uptake, was also observed. In general, a sufficient supply of major nutrients increased plant tolerance to F.⁴⁷ Mutual pollution by SO₂ and F is reported to cause more significant damage to pine trees than changes induced separately by these pollutants.⁶⁶³ The reactions of plants exposed to F pollution, even before any visible symptoms of F toxicity occur, are (1) retarded growth, (2) inhibited reproduction, and (3) yield reduction. However, the most significant effect of increased F concentrations in plants is toxicity to animals. Thus, the F content of forage crops seems to be of greater ecological concern than that of other plants. However, recent findings of increased F levels in food plants, especially of fluoro-organic residues in several vegetables, indicate a possible toxicity to man.⁵³⁹

The best-documented plant responses to F are foliar symptoms such as chlorotic and necrotic lesions and deformation of fruits. These symptoms are not specific, and mimicking symptoms induced by other agents as well as the increased susceptibility of F-polluted plants to microbial diseases were observed by Treshow⁸⁰⁵ and Weinstein.⁸⁵⁷

Plants exhibit a broad range of tolerances to foliar injury by F pollution. Plants that are commonly listed as tolerant plants are asparagus, bean, cabbage, carrot, and willow; while barley, corn, gladiolus, apricot, pine, and larch are classified as susceptible. However, a great variability in plant response to the F accumulation in tissues is observed, even between cultivars or genotypes of the same species. The response of plants is also highly dependent on several environmental and biologic factors. Based on Weinstein's report,⁸⁵⁷ it can be generalized that susceptible plants could be injured by foliar F concentrations that ranged between 20 and 150 mg/kg, intermediate plants can probably tolerate an F content in excess of 200 mg/kg, and highly tolerant plants do not exhibit injury below 500 mg/kg. The toxicity limits for F in orange leaves range from 75 to 125 mg/kg, and some trees of orchards in Spain have F greater than this limit.¹²¹⁰

The effects of plant F on humans and, particularly, on animals are of the greatest concern. Opinions vary as to the toxic threshold values of F in forage, but 30–40 mg/kg is commonly reported.^{166,288,766} More tolerant animals (e.g., lambs and turkeys) may tolerate a higher F concentration in their rations. Direct ingestion of sludge and soil with elevated levels of F by grazing cattle may be also an important source of dietary F.

3 Concentrations in Plants

Fluorine contents of plants have been investigated for a number of reasons such as assessing its hazard to grazing animals, the diagnosis of plant injury, and for monitoring airborne F pollutants. Higher concentrations of F have usually been reported for the aerial parts of plants. Mean F contents of plants grown in uncontaminated areas are very unlikely to exceed 5 mg/kg (Table 22.4). However, in some vegetables, for example, spinach leaves, its concentration may reach up to 28 mg/kg.

According to general opinion, plant F seems to be positively correlated with the concentration of F in rainwater. Davison et al.¹⁷³ discussed a method of the prediction of F concentrations in pasture using multiple regression techniques and including data on aerial deposition of F and rainfall. Several plants, especially forage vegetation, when growing in polluted areas are reported to contain large amounts of F (Table 22.5). Most of the F pollution is likely to be deposited on the leaf surface, which was shown by findings of Fuge and Andrews.¹⁰⁰¹ They reported that F in unwashed grasses from an area of china clay industry ranges from 756 to 3240 mg/kg, whereas F ranged from 330 to 1410 mg/kg in grasses from the same area, but washed in distilled water. Results of the pot experiment clearly indicate that soil F is not an important source of this element to red maple and orchard grass.¹²⁴³ Pine needles are common and good indicators for the F pollution. Pine needles from the

TABLE 22.4
Fluorine in Food and Forage Plants from Various Countries (mg/kg)

Plant	Range	Mean
Wheat, grains	0.4–1.4	0.9
Barley, grains	0.5–5.5	—
Oats, grains	0.2–0.9	0.5
Spinach, leaves	1.3–28.3	—
Lettuce, leaves	4.4–11.3	—
Onion	—	3
Potato, tubers	0.1–3	1.4
Apple, fruits	1.3–5.7	—
Pears, fruits	2.1–4.4	—
Forage legumes, tops	1.5–7.8	4.4
Grass, tops	3–6.8	—

Source: Data compiled by Kabata-Pendias, A. and Pendias, H., *Biogeochemistry of Trace Elements*, 2nd ed., Wyd. Nauk PWN, Warsaw, 1999, 400 (Po).

TABLE 22.5
Excessive Levels of Fluorine in Plants Grown in Contaminated Sites (mg/kg)

Site and Pollution Source	Plant and Part	Maximum or Range of Content	Country	Reference
Mine waste	Grass, tops	130–5450	Great Britain	146
Al-processing industry	Vegetation, foliage	396	Canada	478
	Shrub, ^a leaves	150–500	Australia	557
	Cereals, grains	14–36	Poland	63
	Clover, tops	14–173	Poland	768
	Grass, tops	1330	Czech Republic	500
	Grass, tops	75–340	Poland	381
	Birch, leaves	230	Norway	261
	Pine, needles	48	Norway	261
	Lichens	27–241	Great Britain	606
Brick kilns	Pasture plants	160	Great Britain	166
China clay industry	Grass, ^b tops	576–3240	Great Britain	1001
Fiberglass plant	Vegetation, foliage	945	Canada	478
Phosphate rock processing	Tree, ^c foliage	71–900	Canada	782
	Vegetation, foliage	70	Canada	478
	Sagebrush, tops	100–360 ^d	Russia	278
	Pine, needles	60	Russia	923
Fumigation with F	Alfalfa	1327	—	857
	Grass	496	—	857

^a *Melaleuca nodosa*.

^b Unwashed samples.

^c Balsam fir.

^d AW basis.

vicinity of an aluminum smelter contain F above 1000 mg/kg, while the background value for F in pine needles in Poland is below 20 mg/kg.¹²⁶⁰ Geebelen et al. (2005) used transplanted lichens as biomonitors for atmospheric F pollution and observed the F accumulation up to 243 mg/kg near the F point source. Some parts of plants, growing in acid soils, accumulate increasing amounts of F with time, such as in the case of old tea leaves, which contain up to 300 times more of this element than young leaves (Siemiński, 2001).

II CHLORINE

A INTRODUCTION

Chlorine is a common halogen element in the terrestrial environment. Its average content of the Earth's crust is estimated as 640 mg/kg (Table 3.2). Cl concentrations are very variable, being the highest in igneous rocks, up to 300 mg/kg, and the lowest in sandstone, up to 20 mg/kg. In some calcareous rocks, its concentration may be around 350 mg/kg (Table 22.2). Although Cl is not preferably accumulated by OM, its content, at an average of 41 mg/kg, can be elevated in some coals, up to 8800 mg/kg (Finkelman, 1999).

In a small number of minerals, Cl is present as a major constituent. Some of these are halite, NaCl; carnallite, $\text{KMg}(\text{H}_2\text{O})_6 \text{Cl}_2$; chloroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$; and cerargyrite, AgCl. Most of these minerals are quantitatively unimportant, only halite is relatively abundant, as deposits of solid rock salt, and as dissolved ingredient in seawater and subsurface brines.

Chlorine is a lithophilic element, highly mobile in most conditions and may occur as a minor constituent of various minerals, like amphiboles, apatite, and micaceous and clay minerals. Under specific conditions, mobile Cl^- anions are easily associated with some metals forming minerals such as AgCl, PbCl_2 , $\text{Cu}_2\text{Cl}(\text{OH})_3$, and so on. This element is released during weathering processes, goes into solution as Cl^- ions, and is accumulated in the oceans and seas. Increased Cl levels in recent lacustrine and marine sediments are most probably resulted from organohalogens originated from deposited biogenic material (Müller, 1999).

Yearly global production of Cl was estimated roughly as 40 Mt (Reimann and Caritat, 1998). Salt NaCl, obtained either from solid sedimentary deposits or from seawater and brines, is the prime source of Cl. It is an important raw material and is a prerequisite to the production of soda ash, which is utilized in glass and many chemical products. However, the most common use of NaCl is for household purposes. Processing of several products for daily use, especially associated with some fibers, such as polyvinylchloride (PCV), involves Cl_2 -based materials. In some countries Cl, used as road salt exceeds 50% of its total use.

Chlorine is broadly used as ClO_2 (chlorine dioxide) and utilized principally in the paper pulp and cellulose bleaching. Additional uses are also in bleaching flour, fats, leather, and textiles. In aqueous solution, ClO_2 is used as a sterilizing agent in hospitals, as bactericides, antiseptics, and deodorizers. It is used as a strong disinfectant agent for supplied drinking water, and is also to lower the risk of food contamination during preparation and transport.

Chlorine is a component of several persistent pesticides (fungicides), and of chlorinated organic compounds, such as dioxins/furans and PCBs (polychlorinated biphenyls). The increased use of Cl-pesticides and growing release of polychlorinated hydrocarbons are currently a great threat to the environment and health. All these compounds seem to travel over long distances, concentrated in northern areas and are likely to be accumulated in the fat of mammals. Especially, dioxin load of soils, water, and foodstuffs indicates the capacity of polychlorinated organic compounds to penetrate the environment and to infiltrate the food chain (Coenen, 2004).

B SOILS

The mean Cl content of worldwide soils is estimated as 300 mg/kg, and its highest concentrations are noticed in Cambisols (Table 22.2). In soils of humid climate zones, Cl^- is leached down the

profile and transported with drainage waters. As Bodek et al.⁹⁴⁸ described, almost no soil retention occurs, and therefore Cl in the solution moves through soil at virtually the same speed as the displacing solution. In soils of arid and semiarid climates, on the other hand, Cl⁻ is known to be concentrated in surface horizons. Cl is typically the predominant anion in saline soils. Solonetz and solonchaks are highly enriched with NaCl, as well as in other salts, which are inherited from parent material. Concentrations of Cl in solonchaks usually vary within the order of 0.0X–0.X%.

Elevated levels of Cl⁻ in soil solution (its concentration can reach about X.0%) may influence the behavior of several cations. Hahne and Kroontje¹⁰²¹ calculated that the solubility of Zn(OH)₂ and Hg(OH)₂ is significantly greater in 1.0 M chloride solution than their conditional solubility. However, the greatest environmental concern is associated with Cl affinity for forming soluble and phytoavailable complexes with Cd (Weggler et al., 2004).

Like in a case of other halogens, the distribution of Cl in soils exhibits a clear trend of decreasing concentration with increasing distance from the sea. Låg and Steinnes⁴⁴⁵ found in Norwegian forest soils close to the sea, a Cl range from 475 to 1806 mg/kg with an average of 920 mg/kg, while soils farther from the sea contained Cl within the range of 174–375 mg/kg with an average of 265 mg/kg. Yuita et al.¹¹⁹⁴ also found that Cl in Japanese forest soils (in surface horizons) from the coastal plain ranges from 91 to 486 mg/kg, at the average of 228 mg/kg, while in soils from upland fields, Cl ranged from 56 to 305 mg/kg, at the average of 114 mg/kg.

Excessive amounts of salt (NaCl) applied to soils has resulted in increasing environmental concern.¹¹⁵⁹ Salt-affected soils due to anthropogenic activities are results of several processes: (1) application of de-icing salt to roadways; (2) field irrigation with highly mineralized waters; (3) salt water spills associated with the extraction of oil; and (4) some coal burning. Wind erosion of salt evaporates is also known to affect the Cl enrichment in soils. Several chlorinated dioxins, of natural origin, were found in remote peat bogs in Canada (Gribble, 1999).

C PLANTS

The availability of Cl to plants is related to the associated cations. The Cl⁻ ions are more readily absorbed in the presence of monovalent cations than di- and trivalent cations. The soluble Cl fraction in soils is taken up passively by roots, and is easily transported in plants. Cl can also be absorbed directly by plant leaves from aerial sources, and some plant species are capable of extracting their total Cl requirements from aerial sources via their leaves. Plants may accumulate relatively large amounts of Cl, especially halophytes occurring in coastal regions and in arid or semiarid climate zones.

Chlorine is considered a micronutrient for higher plants. Plants require a relatively low level of Cl for metabolic processes. It plays a role in photosynthesis and is significantly concentrated in chloroplasts. However, the requirement for Cl in photosynthesis remains in doubt.¹¹⁸⁴ This anion also participate in phosphorylation processes and in the activity of cytochromoxidase.⁹⁴³ Organochlorines are biosynthesized by various plants. Cl deficiencies are not observed often, but may occur when plants are growing in soils with Cl contents below 2 mg/kg. Generally, Cl is present in sufficient quantities in most soils to meet its requirement for crops. However, for some crops (e.g., tobacco), the Cl level of 10–15 mg/kg in soils is beneficial. Common symptoms of Cl deficiency are chlorotic leaves and brown edges.

Chlorine contents are reported to be about 10–20 mg/kg in cereal plants. In sugar beet leaves, the Cl range is 100–200 mg/kg, and in potato tubers from 1300 to 5500 mg/kg.⁹⁴³ Several other plants can also contain high levels of Cl, depending on growth conditions. For example, leaves of coconut palm growing at distances up to 25 km from the sea coast contain Cl up to 7000 mg/kg.⁹⁴³ Elevated concentrations of Cl in plants of the city of Yerevan (Armenia), up to 3300 and 3550 mg/kg in tree leaves and vegetable fruits, respectively, are affected mainly by industrial pollution (Nersisyan, 2007).

Toxic Cl levels in plants vary depending on plant tolerance. Bergman⁹⁴³ reported that a general threshold concentration of Cl is 2700 mg/kg. Plants may suffer from too high Cl contents in soil

solutions or water cultures. The less tolerant plants (e.g., beans, apple trees) are inhibited by Cl concentrations from 460 to 673 mg/L, whereas resistant plants (e.g., tobacco, cereals, tomato, cotton, beets, spinach) can grow at Cl contents from 887 to 3546 mg/L. The most toxic to plants are HCl and Cl₂ gases emitted from industrial sources. Strong necrosis of leaf edges is the most common symptom of these injuries. High levels of Cl associated with KCl fertilization can also adversely affect crops, in particular owing to the formation of mobile complexes with Cd.

III BROMINE

A INTRODUCTION

Abundance of bromine in the Earth's crust is about 2 mg/kg and it is relatively uniformly distributed among igneous rocks, within the range of 0.2–4.5 mg/kg, whereas in argillaceous sediments, it is likely to be concentrated up to 10 mg/kg (Table 22.2). Minerals containing Br are not very common, owing to its low abundance and high solubility. The common minerals are bromyrite, AgBr; embolite, Ag(Cl,Br); and iodobromite, Ag(Cl,Br,I). The close correlations of Br and Cl in various rocks have often been observed. Br is very volatile element and its salts are readily soluble and mobile in most environments. However, it is likely to be accumulated by coals and OM. Its concentrations in the U.S. coal average 9.1 mg/kg, but can reach 160 mg/kg (Finkelman, 1999).

Bromine is very reactive chemically and can have several valence states (Table 22.1). However, as the one-electron atom it can form only compounds with oxygen (e.g., Br₂O, BrO₂, BrO₃). Reactive Br species of anthropogenic origin, as well as other halogens, affect ozone by directly destroying it and by reducing its production (von Glasow et al., 2004).

World total (rounded) Br production in 2008 was estimated as 398 kt (USDI, 2009). The major commercial source of Br is seawater; usually recovered as a by-product during evaporation to produce salt.

The primary great use of Br was as ethylene dibromide in gasoline antiknock additive, together with lead. Due to recent environmental legislation, Br addition to gasoline has been significantly reduced.

Considerable amounts of Br (methyl bromide and ethylene dibromide) are used in agriculture as pesticides (fungicide, herbicide, and insecticide). It is utilized in the pharmaceutical industry. The persistent chemical, polybrominated diphenol ethers (PBDEs), is presently broadly used as flame retardants in a great variety of products. Br is also used in photosensitive compounds, in photographic industries.

All bromine-based compounds are very persistent and seem to travel over long distances in both the atmosphere and water.

B SOILS

There are only few reports on the Br status of soils indicating its average content of soils as 10 mg/kg (Table 3.2). The lowest range of Br, from 7.9 to 8.2 mg/kg, was found in Podzols of Poland, and the highest, up to above 100 mg/kg, in volcanic ash soils (Table 22.2). The reference soils from China contain Br within the range of 2.6–7.2 mg/kg, and soils from the United States, between 1.4 and 7.8 mg/kg.¹³¹³ Average Br status in soils of Finland amounts 10 mg/kg, at the 90th percentile range.¹³⁶⁸ Somewhat similar value of arithmetic mean, 5.7 mg/kg, was estimated for surface soils of Austria.¹³⁰⁸

Observed increased Br contents in soils close to sea coasts is an effect of Br evaporation from sea. Yuita¹¹⁹⁴ reported that soils at the Sea of Japan accumulated Br up to 495 mg/kg. Soils derived from volcanic ash contain increased amounts of Br due to both elevated Br contents in parent material and impact of volcanic exhalation.

Anthropogenic sources of Br in soils are associated with the impact of car exhaust, (when ethylene dibromide was added to gasoline) and with broad use of Br-pesticides. Due to these practices,

soil Br could increase significantly, and particularly in soil solution, since these Br compounds can be easily transformed to very mobile Br^- anionic form. Carbon and SOM are known to accumulate Br, and a strong correlation of Br with OM is reported for both superficial sediments and soils.^{855,875}

Soil fumigation with methyl bromine can result in almost complete eradication of population of a wide variety of soil microflora and fauna and thus alter the trophic structure of soils (Pavelka, 2004).

Låg and Steinnes⁴⁴⁵ assumed that Br enrichment in topsoil horizons is principally an effect of its precipitation with rain. This conclusion is supported by the findings of Yuita et al.⁸⁹⁷ that a considerable part of the Br accumulated in soils of the temperate monsoon climate is directly due to the long retention period of Br from rainwater by soils. Despite the observed sorption capacity of hydroxides of Al and Fe, OM and clays for Br, it is known as the element most easily leached from soil profiles, and its transportation to ocean basins in large amounts is often reported.

C PLANTS

Although Br is reported to occur in all plant tissues, it is not yet known whether it is essential for plant growth. The mean Br content of plants seems not to exceed about 50 mg/kg, and some higher values should apparently be related to pollution. Higher Br contents, above 100 mg/kg, are in legumes and grass (Table 22.6). Stärk et al.⁷⁵³ found that Br was usually higher in leaves than in roots and that it was easily soluble from tissues. Wilkins⁸⁷⁵ concluded that Br concentrations in herbage do not correlate with its contents of soils or with soil parameters. However, plants are known to take up Br readily when grown in soils enriched with Br. Wyttenbach et al.¹⁵⁵³ found a high concentration of Br in Norway spruce needles at polluted and maritime sites, and very low at continental prealpine sites. The mean Br value in spruce needles from remote continental sites was 0.1 mg/kg.

According to Yamada,⁸⁹⁰ plants grown in volcanic ash soil contain Br up to 2000 mg/kg. Staerk and Suess⁷⁵¹ reported Br concentrations from 267 mg/kg in celery roots to 9515 mg/kg in lettuce leaves that were cultivated in a greenhouse after fumigation with CH_3Br , at the rate of 75 g/m³. Methyl bromide and other Br organic compounds used as fumigants for soils, grains, and fruits may be serious sources of Br in human diets.

TABLE 22.6
Bromine in Food and Forage Plants from Various
Countries (mg/kg)^a

Plant	Range	Mean
Barley, grains	2.1–6.4 ^b	5.5
Oats, grains	—	3.1
Triticale, grains	—	33.0
Beans, seeds	—	15
Lettuce, leaves	20–22	—
Cucumber, fruits	—	—
Potato, tubers	10–20	—
Radish, roots	4.2–14.2	—
Celery, stalks	24–26	17
Forage legumes, tops	—	—
Grass, tops	2.1–52	—
Mushrooms ^c	3–119	—
	2–36	—

^a From various sources, after Kabata-Pendias and Pendias.¹³⁵⁷

^b For inland and coastal regions, respectively.

^c Kind not specified.

Since Br^- can substitute for part of the Cl^- requirement of plants, its excess may be toxic to plants. Plant species differ in their tolerance to soil Br; several vegetables and flowers are known as sensitive plants (e.g., potato, spinach, sugar beet, onion, carnation, chrysanthemum). Symptoms of the Br toxicity resemble excess salt effects; so chlorosis followed by leaf tip necrosis is the common feature. As Gough et al.²⁷⁹ reviewed, citrus seedlings may be satisfactorily used as an indicator of Br toxicity since the reduction in their growth correlates positively with water-soluble soil Br. Plants resistant to the Br toxicity (carrot, tobacco, tomato, celery, melon) can accumulate Br above 2000 mg/kg, without showing any effects. Marine plants, in general, contain more Br than do land plants.

IV IODINE

A INTRODUCTION

Iodine content of the Earth's crust is extremely variable; however, its crustal average abundance is estimated as 0.5 mg/kg (Table 3.2). Its highest content is in sedimentary rocks; up to 38 mg/kg in argillaceous sediments and up to 17 mg/kg in organic-rich shales. Igneous acid rocks contain I up to 0.5 mg/kg (Table 22.2). The high average I contents of 30 mg/kg in deep-sea carbonates are reported by Muramatsu and Wedepohl.¹⁴³⁴

Iodine does not form many own minerals, but can occur as minor constituent of various minerals. Its associations, such as CuI and AgI , can be found in weathering zones of these metal deposits. Iodates are rare minerals occurring only in very arid regions, and their structures are not completely understood. Anhydrous iodates are lautarite, $\text{Ca}(\text{IO}_3)_2$ and bellingerite, $\text{Cu}_3(\text{IO}_3)_6 \cdot 2\text{H}_2\text{O}$; and iodate with hydroxyl: is salesite, $\text{Cu}(\text{IO}_3\text{OH})$. Other minerals, such as iodoargirite, AgI ; marshite, CuI ; and dietzite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{CrO}_4$ are much less common.

Increased I contents in some phosphates, bituminous shales, and coal are associated with OM. It is concentrated in some nitrate deposits, especially in Chile saltpeter, up to around 400 mg/kg. The suggestion of an atmospheric origin of this element seems to be most reasonable. I, when heated, sublimates and goes from a solid directly to a vapor phase, without the liquid phase. One of its features is a volatilization from seas as CH_3I and I_2 .

During weathering, I is rapidly released and transported to ocean and sea basins. Most of the I, nearly 70%, exists in ocean sediments. The I geochemistry, a biophile element, is strongly connected with its involvement in biological processes. High I contents of sediments and soils is mostly due to its uptake by plankton or is due to the fixation by OM. As Prince and Calvert⁶³² stated, sediments of reducing environments contain greater amounts of I than do oxidized sediments.

The global production of I in 2008 was around 27 kt (USDI, 2009). It is primarily received from brines that are associated with gas and oil deposits. Until 1959, ash of seaweeds was the important I source. Caliche (surface layers of some calcareous deposits) is presently the most economic I source.

Iodine is applied in a number of chemicals and pharmaceuticals. In chemistry, I compounds are used as catalyst. It is added to colorants and inks, and as AgI , a photosensitive compound, is used in photography. Its organic compounds are used both externally and internally in medicine. The Iodine Deficiency Disorders (IDD) is a relatively common health problem, especially in Africa and Asia. It has been estimated that about 30% of the world's population are affected by the I deficiency (Blasco et al., 2008). Chandrajith et al. (2005) discussed the I deficiency problem in Sri Lanka and concluded that IDD problems of the population is not closely associated with I concentration of soils. Health aspects of the I deficiency in the food chain is broadly reviewed by Nordberg and Cherian (2005).

B SOILS

The mean I contents of worldwide soils is estimated as 2.8 mg/kg (Table 3.2). However, its concentrations vary widely from <0.1 to 10 mg/kg. In volcanic ash soils its content may be elevated up to

above 100 mg/kg (Table 22.2). Most commonly, soils contain several times as much I as do parent rocks. Its accumulation in surface and subsurface soil horizons is affected by aerial deposition and biogenic concentration. It has been stated that the atmosphere is a basic source of I in soils. The ocean is the reservoir from which all of the atmosphere I is drawn.

The highest I concentrations are in Cambisols. In some soils of islands (Ireland, Japan, New Zealand) as well as in sea-coast areas, higher I accumulations, up to around 150 mg/kg are reported. The mean I content of peat in the United Kingdom is 46.8 mg/kg (Whitehead *vide* Fuge, 2005). Also volcanic ash soils usually contain elevated amounts of I, up to 104 mg/kg, and solonchak soils of arid and semiarid regions, up to 340 mg/kg.¹³⁵⁷ The I ranges in the reference soils of China from 1.3 to 19.7 mg/kg, and in the United States soils, from 1 to 35 mg/kg.¹³¹³ In Russian chernozems, I varies from 4 to 5.6 mg/kg, being accumulated in the top layer.¹¹²³ The mean I contents in paddy soils from Sri Lanka vary from 0.13 to 1.0 mg/kg in areas of low and high IDD symptoms in the population, respectively, and seem to be not the most important factor controlling this health disorders (Chandrajith et al., 2005).

It is most unlikely that I occurs in soils in the form of I minerals. The association between I and SOM, hydrous oxides of Fe and Al, and clay of the chlorite–illite group was often observed.^{402,868} However, as Selezniev and Tiuriukanov⁷⁰⁰ and Whitehead⁸⁶⁸ reported, OM is most responsible for the I sorption in soil and therefore I is accumulated mainly in topsoil horizons. Soil microorganisms are believed to play a significant role in the I cycle, owing to their great capability to accumulate this element. Letunova et al.¹⁰⁶² calculated that the microorganism biomass contains 0.012–3.24% of the I present in surface soil layers. Some fungi occurring in soils (e.g., *Penicillium chrysogenum*) are known to accumulate even much higher amounts of I. Amount and kind of OM, as well as fixation by microorganisms, play an important role in the increased fixation of this element. Dai et al. (2004) reported that iodate (IO_3^-) adsorption is negatively correlated with SOM and positively with free Fe oxides, whereas no correlation exists between iodate adsorption and CEC and soil pH. Yamada et al. (1999) distinguished four fractions of I in soils. There are fractions bound to HA and FA, and iodate and iodine species. In general, large proportions of I in soils occurred in organically bound forms.

The influence of soil reaction on the I status is diverse. Soil acidity favors the I sorption by soil components. On the other hand, in alkali soils of arid and semiarid regions, I is known to be greatly accumulated (e.g., in solonchak, up to 340 mg/kg) due to both salinity processes and a low degree of the I mobilization under alkaline pH conditions (Anikina³⁰). I abundance in soils shows a relation with their texture, but as Gerzabek et al.¹³⁰⁸ described, I is positively correlated only with clay contents of noncalcareous soils, whereas in calcareous soils the relationship was observed for several soils parameters, for example, clay, exchangeable calcium and organic carbon. Usually, light soils of humid climate regions are poor, whereas clayed soils are enriched with this element. However, this may vary greatly because I levels in soils are highly dependent on the atmospheric precipitation. The distance from the sea and recent glaciation's sediments (Pleistocene) also have an influence on the soil I status.

The alteration of I species, especially the oxidation of iodide to iodate occurs in soils. Also, reductive reactions of IO_3^- , due to SOM impact and microbial activity cause the formation of I_2 in soils. The exchange of volatile iodine compounds between soils and atmosphere is relatively a common process. I species occurring in the aquatic phase of soil are mainly following anions: I^- , I_3^- , IO_3^- , and H_4IO_6^- , of which the first two are most common (Kabata-Pendias and Sadurski, 2004). The absorption rate differs for the I species and is higher for I^- than for IO_3^- (Yuita¹¹⁹⁴). According to Yamaguchi et al. (2006), I^- in contact with the soil was not likely to be oxidized to IO_3^- under aerobic incubation. I was leached out in soil solution as I^- under anaerobic conditions, whereas part of I species was retained by soil as I_2 or organoiodine under both anaerobic and aerobic conditions. According to Chandrajith et al. (2005), the I concentration in paddy soils is controlled by water regime and landscape, as well as by the OM content. Although I is scarcely mobile under most soil conditions, in some extreme conditions (e.g., submerged soil) it can be highly mobile, and thus

available to plants. However, Fuge and Johnson¹⁰⁰² reported that only a small fraction of the total I is easily mobile in soils. The relative proportion of mobile I (cold or hot water extractable) ranges from <1 to 25% of its total content in soils. Thus, most of the I occurs in fixed forms being sorbed by humic and fresh OM, as well as being fixed in or on clays and crystal lattice of minerals.

The I behavior in soils has been studied in relation to its availability to plants. Hartmans³⁰⁸ and Whitehead⁸⁶⁹ reported relatively few effects of chalk, N, and P on the I uptake by plants. However, liming is known to reduce the solubility of iodides, iodates, and iodine in soils and thus also to reduce I bioavailability. When I was applied to peat soils, only about 4% of the added amount was taken up by plants.

Soils in surroundings of fossil fuel combustion plants and, previously common, kelp burning facilities, as well as in the close vicinity to high traffic roads have elevated I levels. Some sewage sludge applied on fields also can add this element to surface soil.

C PLANTS

Iodine has not been shown to be essential to plants, and some reports on its stimulating effects, at low concentrations, on plant growth have not been explained. Mengel and Kirkby⁵³¹ wrote that the stimulating effect of I was observed at the concentration of 0.1 mg/kg in nutrient solutions, whereas toxic effects occur at the concentration of 0.5–1.0 mg/kg. The toxic concentration is higher than the normal soluble I content of soils; therefore, I toxicity is seldom present in plants under natural field conditions. Yuita¹¹⁹³ reported, however, a physiological disease of rice plants, “Akagare,” induced by the excessive absorption of I from soils enriched with easily soluble I when the land was converted for submerged paddy fields.

Opinions seem to differ regarding the relation between the I content of plants and its status of soils, but apparently the variation in I contents of plants appears to be generally unaffected by soil kind and type. On the other hand, some data cited by Fuge and Johnson¹⁰⁰² show a marked variation of I content of spruce and larch twigs with soil type. Also, data presented by Anke et al. (2007) after Antal et al. (2005) clearly indicate the influence of geological soil origin on I concentrations in medicinal herbs (Table 22.7). Thus, both parent material and the distance from the North Sea influence the I contents of plants.¹⁰¹⁷

In general, the phytoavailability of I is low since, most often, strongly bound I will not be neither available to roots nor easily volatilized from soils. As Fuge (2005) reported, the SPTF values of I are within the range of 0.01–1.5, and mainly between 0.01 and 0.1.

Soluble forms of I seem to be easily available to plants; therefore, terrestrial plants contain much less I than do marine plants, which are known to concentrate I from 53 to 8800 mg/kg.⁷⁰⁹ As Muramatsu et al. (1983) described, plants take up I relatively easily from the soil solution, and iodine (I^-) is much more available species than iodates (IO_3^-). Both I species are more concentrated in roots than in shoots which could be due to the absorption onto the root surface. The mechanism

TABLE 22.7
Iodine Content of Medicinal Plants from Various Geological Sites (mg/kg)

Parts of Herbs	Geological Origin of Parent Material			
	Alluvial Deposit	Limestone	Phyllite	Granite
Total plant	1.21	0.98	1.15	0.84
Roots	1.67	1.20	1.06	0.28
Leaves	0.84	0.86	0.61	0.68
Flowers	1.04	0.75	0.20	0.49

Source: Data from Antal D.S. et al. 2005. *Sveikatos mokslai* 39:86–91.

of I uptake by plants is not understood. According to Selezniev and Tiuriukanov,⁷⁰⁰ organically bound I is scarcely available to cultivated plants, but after the decomposition of SOM by bacteria, soil I becomes phytoavailable.

Strzetelski et al. (2008) reported that the most effective was KI form in the biofortification of spinach (*Spinacia oleracea* L.), used both as soil and/or foliar application. The stimulating effect of KI application on the NO_3^- accumulation by spinach was observed. These authors (Strzetelski et al., in press) reported elevated levels of vitamin C in radish (*Raphanus sativus* L.) after KI treatment, observed in their experiments similar to those observed by other authors. Smoleń (2009) investigated an impact of KI and KIO_3 applications on some TE levels in carrot. Depending on KI forms effects varied and resulted in both increased (Cr) or decreased (Co, Mn, Sr) contents. However, other factors, such as mineral fertilizers, modified the KI impact on TE concentrations in carrot.

Muramatsu et al.¹⁴³⁷ studied the volatilization of ^{129}I from the soil-plant system and observed a marked emission of this radionuclide, in a methylated form (CH_3I), from the rice plant shoot into the atmosphere. It was presumed that I in the flooded soil was methylated by the action of roots or microorganisms.

Shacklette and Cuthbert⁷⁰⁹ studied the I distribution among a variety of plant groups from various soils and stated that although I contents of individual plant species may vary considerably, the range in amount seems to be a species characteristic. Generally, vegetables and fleshy mushrooms contain more I than other land plants (Table 22.8). Relatively higher I contents is given by Anke et al. (2007) for fodder plants (mean value in mg/kg): (1) 0.102, fescue grass; (2) 0.133, red clover; (3) 0.197, lucerne; and (4) 0.319, fodder beets. However, Antal et al. (2005) emphasized that medicinal plant species contain usually 10–100 times more I than do food plants.

TABLE 22.8
Iodine in Food and Forage Plants from Various Countries (mg/kg)

Plant	Range/Mean	Reference
Barley, grains	0.005–0.038 ^a	441
	3.4–7.1	709
Snap beans, pods	5.7–9.5	709
Cabbage, leaves	9–10	709
Lettuce, leaves	<0.01 ^b	709
Asparagus, stems	5.6–5.9	574
Carrot, roots	0.025	709
Onion, bulbs	7.8–10.4	709
Potato, tubers	2.8–4.9	709
Apple, fruits	<0.003	574
Orange, fruits	<0.01	574
Grass tops	0.10–0.28	166
	<1–4 ^c	221
	0.3–1.6	316
	4.3–7.1	709
	0.03–0.08	386
Clover, tops	0.14–0.44	166
	0.11–0.5	316, 1017
	0.06–0.12	386
Mushrooms	5.2–9.5	709

^a For inland and coastal areas, respectively.

^b FW basis.

^c For low and high I areas, respectively.

Some authors reported a higher I contents in tops than in roots.^{166,230,308} The I levels show also seasonal variation, and its lowest contents were noticed during the summer season: for example, its content of green wheat sampled in April and June was 0.215 and 0.068 mg/kg, respectively (Anke et al., 2007). The highest I concentrations are in algae and seem to be associated with the pigmentation; for example, algae contain, on average (in mg/kg): green 5; red 380; and brown 3490. About 65% of total I in algae is bound to proteins.¹³³³

Plants are capable of absorbing I directly from the atmosphere, both through the cuticle and as adhesive particles on the surface of hairy leaves. The atmospheric I can contribute significantly to the I content of plants. Gurievich²⁹⁵ reported that in the Baltic regions, higher plants accumulated I to as much as 40–50 mg/kg, and mosses contained 360–410 mg/kg. However, Rühling et al.¹¹³⁵ gave a quite different range for I in mosses from the Scandinavian countries, within the range of 1.5–3.5 mg/kg.

Adequate I levels in food and feed plants are required in human and animal nutrition; therefore, some scientists have investigated the I as a fertilizer for soil or foliar application.¹⁶⁶ These techniques, however, do not appear to be of any practical importance. Blasco et al. (2008) increased the I level in lettuce leaves by adding iodide and iodate compounds to a hydroponic cultivation.

The I toxicity to plants due to pollution is not often reported. As Gough et al.²⁷⁹ reviewed, large applications of kelp to soil as fertilizers (practiced on some coastal fields) may cause symptoms of the I toxicity which are similar to those caused by Br excess: margin chlorosis in the older leaves, while the younger leaves become dark green.

D IODINE ISOTOPES

Among many I isotopes, the only stable isotope in nature is ¹²⁷I. Two radioactive isotopes, ¹²⁹I and ¹³¹I, are the most common by-products of atomic reactors and nuclear weapons testing, and have been released in various proportion into the environment. The half-lives of these isotopes vary from 8 days (¹³¹I) to 1.6×10^7 years (¹²⁹I), and both are of growing environmental and health concern. However, ¹²⁹I is also a naturally occurring long-half-life radioisotope. The ¹²⁹I/¹²⁷I ratio is used as hydrological, geochemical, and environmental tracers.

The occurrence of both radionuclides, ¹²⁹I and ¹³¹I, in soils has recently become of a great environmental concern, especially after the reactor accident in Chernobyl in 1986. The impact of the ¹³¹I emission from the Chernobyl reactor can be illustrated by its levels in soils near Warsaw (Poland); a few days after the accident, the level of its radiation was 19.9 kBq/m², and 2 weeks later was 3.7 kBq/m² (Grabowski et al.¹³¹⁵). Schimmack et al.¹¹⁴⁰ observed a relatively fast migration of ¹³¹I down the soil profile after its deposition by the fallout from the reactor accident in Chernobyl.

The emission of much more stable ¹²⁹I has slowly continued from different sources, which can be easily observed in the increasing ratio of ¹²⁹I to stable ¹²⁷I in soils and other compartments of the environment.^{1434,1468} Koch and Kay¹⁰⁵³ studied the transportability of the long-lived and potentially hazardous nuclide ¹²⁹I in organic soil. The proportion of I losses from the solution phase differs widely with the kind of OM used in the experiment. The authors concluded that the long-term processes that operate in the field to immobilize I are highly variable between soils and within a large body of a soil. Muramatsu et al.¹⁴³⁷ observed that ¹²⁹I⁻ added to soils is readily sorbed in the soil solid phase. However, it is slowly desorbed into soil solution with passing time, and under the enhancing impact of organic substances. Ligands iodide alone or in admixture with other extractants are proposed to be used as washing agents for trace metal desorption from a contaminated soil (Shin et al., 2005).

For the assessment of the impact of nuclear techniques on the level of radioisotopes of I in surface soils, data are necessary on ¹²⁹I, the only naturally occurring radioisotope, and on the ratio of ¹²⁹I:¹²⁷I. As Muramatsu et al.¹⁰⁹⁶ reported, some ¹²⁹I is also added to the environment due to nuclear weapons tests, and therefore the ratio of ¹²⁹I to stable ¹²⁷I has increased in recent times in orders of magnitude from 10^{-12} to about 10^{-8} .

Appendix

The following are common plant names used in this book, with corresponding Latin names, and families (within parentheses) to which they are assigned.

Alamo switchgrass, *Panicum virginatum* L. (Graminaceae)
Alfalfa, *Medicago sativa* L. (Leguminosae)
Amarant, *Amaranthus hypochondriacus* L. (Amaranthaceae)
Apple, *Pyrus malus* L. (Rosaceae)
Apricot, *Prunus americana* L. (Rosaceae)
Asparagus, *Asparagus officinalis* L. (Liliaceae)
Avocado, *Persea americana* Mill. (Lauraceae)
Barley, *Hordeum vulgare* L. (Gramineae)
Bean, *Phaseolus* sp. (Leguminosae)
Beech, *Fagus* sp. (Fagales)
Birch, *Betula* sp. (Betulaceae)
Black gum, *Nyssa silvatica*
Blueberry, *Vaccinium* sp. (Ericaceae)
Brazil nuts, *Bertholletia excelsa* (Lecythidaceae)
Broccoli, *see* Brussels sprouts
Bromegrass, *Bromus* sp. (Gramineae)
Broomsedge, *Andropogon* sp. (Gramineae)
Brussels sprouts, *Brassica oleracea* var. *gemmifera* Zenker (Cruciferae)
Buckwheat, *Fagopyrum sagittatum* Gilib. (Polygonaceae)
Bush bean, *Phaseolus vulgaris* L. (Leguminosae)
Cabbage, *Brassica oleracea* var. *capitata* L. (Cruciferae)
Carnation, *Dianthus caryophyllus* L. (Caryophyllaceae)
Carrot, *Daucus carota* L. (Umbelliferae)
Cauliflower, *Brassica oleracea* var. *botrytis* L. (Cruciferae)
Celery, *Apium graveolens* var. *dulce* DC. (Umbelliferae)
Chard, *Beta vulgaris* var. *cicla* L. (Chenopodiaceae)
Cheatgrass, *Bromus secalinus* L. (Gramineae)
Cherry, *Prunus avium* L. or *P. cerasus* L. (Rosaceae)
Chicory, *Cichorium intybus* L. (Compositae)
Chinese cabbage, *Brassica pekinensis* Lour., Rupr. (Cruciferae)
Chive, *Allium schoenoprasu* L. (Liliaceae)
Chrysanthemum, *Chrysanthemum* sp. (Compositae)
Clover, *Trifolium* sp. (generally, *T. pratense* L.) (Leguminosae)
Coconut palm, *Cocos nucifera* (Arecaceae)
Collard, *Brassica oleracea* var. *viridis* L. (Cruciferae)
Comfrey, *Symphytum officinale* L. (Boraginaceae)
Corn, *Zea mays* L. (Gramineae)
Cotton, *Gossypium* sp. (Malvaceae)
Cottonwood, *Populus angustifolia* (Salicaceae)
Cucumber, *Cucumis sativus* L. (Cucurbitaceae)
Dandelion, *Taraxicum officinale* Weber (Compositae)

Douglas fir, *Pseudotsuga menziesii* (Mirb.) Franco (Pinaceae)
 Elders, *Sambucus nigra* L. (Caprifoliaceae)
 False oat grass, *Arrhenan thenum eliatum* (Gramineae)
 Fescue, *Festuca arundinacea* L. (Gramineae)
 Flax, *Linum usitatissimum* L. (Linaceae)
 Fodder radish, *see* Radish
 Garlic, *Allium sativum* L. (Liliaceae)
 Gladiolus, *Gladiolus* sp. (Iridaceae)
 Grape, *Vitis vinifera* L. or *V. labruscana* Bailey (Vitaceae)
 Hairy milk-vetch, *Oxytropis pilosa* L. (Leguminosae)
 Heather, *Calluna vulgaris* L. (Ericaceae)
 Hickory tree, *Carya* sp. (Juglandaceae)
 Hops, *Humulus lupulus* L. (Moraceae)
 Horse bean, *Dolichos lablab* L. (Leguminosae)
 Horsetail, *Equisetum* sp. (Equisetaceae)
 Indian mustard, *Brassica juncea* L. (Cruciferae)
 Kenaf, Ketnia, *Hibiscus cannabinus* (Malvaceae)
 Kidney bean, *Phaseolus vulgaris* cultivar (Leguminosae)
 Labrador tea, *Ledum palustre* L. (Ericaceae)
 Larch, *Larix* sp. (Pinaceae)
 Lettuce, *Lactuca sativa* L. (Compositae)
 Limber pine, *Pinus flexilis* James (Pinaceae)
 Linden, *Tilia* sp. L. (Tiliaceae)
 Lucerne, *Medicago sativa* L. (Leguminosae)
 Maize, *Zea mays* L. (Gramineae)
 Mangel, *Beta vulgaris* var. *macrorhiza* Hort. (Chenopodiaceae)
 Maple, *Acer* sp. (Aceraceae)
 Marsh bent grass, *Agrostis stolonifera* L. (Gramineae)
 Mother wort, *Artemisia semiarida* L. (Compositae)
 Mushroom, edible fleshy fungus of the Basidiomycetes
 Mustard, *Brassica nigra* (L.) Koch or *B. hirta* Moench. (Cruciferae)
 Narcissus, *Narcissus tazetta* L. (Amaryllidaceae)
 Nettle, *Urtica* sp. (Urticaceae)
 Norway spruce, *Picea abies* [L.] Karts. (Pinaceae)
 Oak, *Quercus* sp. (Fagaceae)
 Oats, *Avena sativa* L. (Gramineae)
 Onion, *Allium cepa* L. (Liliaceae)
 Orange, *Citrus sinensis* Osbeck (Rutaceae)
 Orchardgrass, *Dactylis glomerata* L. (Gramineae)
 Pea, *Pisum sativum* L. (Leguminosae)
 Peanut, *Arachis hypogaea* L. (Leguminosae)
 Perennial ryegrass, *Lolium perenne* L. (Gramineae)
 Pine, *Pinus* sp. (Pinaceae), mainly *Pinus sylvestris*
 Potato, *Solanum tuberosum* L. (Solanaceae)
 Pulses, edible seeds of various legumes
 Radish, *Raphanus sativus* L. (Cruciferae)
 Rape, *Brassica rapa* L. (Cruciferae)
 Raya, *Brassica juncea* Coss. (Cruciferae)
 Red beet, *Beta vulgaris* var. *crassa* Alef. (Chenopodiaceae)
 Red clover, *Trifolium pratense* L. (Leguminosae)
 Red maple, *Acer rubrum* L. (Aceraceae)

Rice, *Oryza sativa* L. (Gramineae)
Rose, *Rosa* sp. (Rosaceae)
Ryegrass, *Lolium perenne* L. or *L. multiflorum* Lam. (Gramineae)
Sagebrush, *Artemisia tridentata* Nutt. (Compositae)
Scots pine, *Pinus sylvestris* L. (Pinaceae)
Sedge, various genera and species of the Cyperaceae family
Sesame, *Sesamum* sp. (Pedaliaceae)
Snap bean, *Phaseolus vulgaris* L. cultivar (Leguminosae)
Sorghum, *Sorghum vulgare* Pers. (Gramineae)
Soybean, *Glycine max* (L.) Merr. (Leguminosae)
Spinach, *Spinacia oleracea* L. (Chenopodiaceae)
Spruce, *Picea* sp. (Pinaceae)
Strawberry, *Fragaria ananassia* Duchesne (Rosaceae)
Sudan grass, *Sorghum sudanense* (Piper) Stapf. (Gramineae)
Sugarbeet, *Beta vulgaris* var. *saccharinum* Hort. (Chenopodiaceae)
Sunflower, *Helianthus annuus* L. (Compositae)
Sweetclover, *Melilotus officinalis* (L.) Lam. or *M. alba* Desr. (Leguminosae)
Sweet corn, *Zea mays* var. *rugosa* Bonaf. (Leguminosae)
Sweet vernal grass, *Anthoxanthum odoratum* L. (Gramineae)
Tagacanth, *Astragalus bisulcatus* L. (Leguminosae)
Tea, *Thea sinensis* L. (Theaceae)
Timothy, *Phleum pratense* L. (Gramineae)
Tobacco, *Nicotiana tabacum* L. (Solanaceae)
Tomato, *Lycopersicum esculentum* Mill. (Solanaceae)
Triticale, an artificial hybrid of wheat and rye
Turkish hazel, *Corylus colurna* L. (Betulaceae)
Turnip, *Brassica napus* L. (Cruciferae)
Valencia orange, *Citrus sinensis* Osbeck cultivar (Rutaceae)
Water hyacinth, *Eichhornia crassipes* L. (Pontederiaceae)
Wheat, *Triticum aestivum* L. (Gramineae)
White clover, *Trifolium repens* L. (Leguminosae)
Willow, *Salix* sp. (Salicaceae)
Wormwood, *Artemisia* sp. (Compositae)

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